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<b>(54) Title:</b> COPOLYMERS OF ETHYLENE AND 1,3-BUTADIENE  <b>(57) Abstract</b> <p>Ethylene copolymers having in their structure cyclopentane rings connected in the 1 and 2 positions. The ethylene copolymers of the invention may be formed from polymerization of ethylene and butadiene and preferably have a pre-dominance of the copolymer units formed as 1,2-cyclopentane units, preferably trans 1,2-cyclopentane. Other butadiene units incorporate 1,2 and cis and trans 1,4 noncyclic.</p>		

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- 1 -

## COPOLYMERS OF ETHYLENE AND 1,3-BUTADIENE

1 Cross Reference:

2 This application is a continuation-in-part of U. S. Patent  
3 Application Serial No. 747,615 filed June 21, 1985.

4 Background of the Invention:

5 This invention relates to a new, improved catalyst useful  
6 for the polymerization and copolymerization of olefins and  
7 particularly useful for the polymerization of ethylene and  
8 copolymerization of ethylene with 1-olefins having 3 or more carbon  
9 atoms such as, for example, propylene, i-butene, 1-butene, 1-pentene,  
10 1-hexene, and 1-octene; dienes such as butadiene, 1,7-octadiene, and  
11 1,4-hexadiene or cyclic olefins such as norbornene. The invention  
12 particularly relates to a new and improved heterogeneous transition  
13 metal containing supported catalyst which can be employed without the  
14 use of an organometallic cocatalyst in the polymerization of  
15 olefins. The invention further generally relates to a process for  
16 polymerization of ethylene alone or with other 1-olefins or diolefins  
17 in the presence of the new supported transition metal containing  
18 catalyst comprising the reaction product of a metallocene and an  
19 alumoxane in the presence of an support material such as silica.

20 Traditionally, ethylene and 1-olefins have been polymerized  
21 or copolymerized in the presence of hydrocarbon insoluble catalyst  
22 systems comprising a transition metal compound and an aluminum  
23 alkyl. More recently, active homogeneous catalyst systems comprising  
24 a bis(cyclopentadienyl)titanium dialkyl or a  
25 bis(cyclopentadienyl)-zirconium dialkyl, an aluminum trialkyl and  
26 water have been found to be useful for the polymerization of  
27 ethylene. Such catalyst systems are generally referred to as  
28 "Ziegler-type catalysts".

29 German Patent Application 2,608,863 discloses the use of a  
30 catalyst system for the polymerization of ethylene consisting of bis  
31 (cyclopentadienyl) titanium dialkyl, aluminum trialkyl and water.

32 German Patent Application 2,608,933 discloses an ethylene  
33 polymerization catalyst system consisting of zirconium metallocenes  
34 of the general formula  $(\text{cyclopentadienyl})_n\text{ZrY}_{4-n}$ , wherein n  
35 stands for a number in the range of 1 to 4, Y for R,  $\text{CH}_2\text{AlR}_2$ ,  
36  $\text{CH}_2\text{CH}_2\text{AlR}_2$  and  $\text{CH}_2\text{CH}(\text{AlR}_2)_2$ , wherein R stands for alkyl

1 or metallo alkyl, and an aluminum trialkyl cocatalyst and water.

2 European Patent Application No. 0035242 discloses a process  
3 for preparing ethylene and atactic propylene polymers in the presence  
4 of a halogen-free Ziegler catalyst system of (1) cyclopentadienyl  
5 compound of the formula (cyclopentadienyl)<sub>n</sub>MeY<sub>4-n</sub> in which n is  
6 an integer from 1 to 4, Me is a transition metal, especially  
7 zirconium, and Y is either hydrogen, a C<sub>1</sub>-C<sub>5</sub> alkyl or metallo  
8 alkyl group or a radical having the following general formula  
9 CH<sub>2</sub>AlR<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>AlR<sub>2</sub> and CH<sub>2</sub>CH(AlR<sub>2</sub>)<sub>2</sub> in which R  
10 represents a C<sub>1</sub>-C<sub>5</sub> alkyl or metallo alkyl group, and (2) an  
11 alumoxane.

12 Additional teachings of homogeneous catalyst systems  
13 comprising a metallocene and alumoxane are European Patent  
14 Application 0069951 of Kaminsky et al, U.S. 4,404,344 issued  
15 September 13, 1983 of Sinn et al., and U.S. Applications 697,308  
16 filed February 1, 1985, 501,588 filed May 27, 1983, 728,111 filed  
17 April 29, 1985 and 501,740 filed June 6, 1983, each commonly assigned  
18 to Exxon Research and Engineering Company.

19 An advantage of the metallocene alumoxane homogeneous  
20 catalyst system is the very high activity obtained for ethylene  
21 polymerization. Another significant advantage is, unlike olefin  
22 polymers produced in the presence of conventional heterogeneous  
23 Ziegler catalysts, terminal unsaturation is present in polymers  
24 produced in the presence of these homogeneous catalysts.  
25 Nevertheless, the catalysts suffer from a disadvantage, that is, the  
26 ratio of alumoxane to metallocene is high, for example in the order  
27 of 1,000 to 1 or greater. Such voluminous amounts of alumoxane would  
28 require extensive treatment of polymer product obtained in order to  
29 remove the undesirable aluminum. A second disadvantage, of the  
30 homogeneous catalyst system which is also associated with traditional  
31 heterogeneous Ziegler catalysts, is the multiple of delivery systems  
32 required for introducing the individual catalyst components into the  
33 polymerization reactor.

34 It would be highly desirable to provide a metallocene based  
35 catalyst which is commercially useful for the polymerization of  
36 olefins wherein the aluminum to transition metal ratio is within  
37 respectable ranges and further to provide a polymerization catalyst

1    which does not require the presence of a cocatalyst thereby reducing  
2    the number of delivery systems for introducing catalyst into  
3    polymerization reactor.

4           There exists a need for new ethylene polymer structures from  
5    various comonomers wherein new/improved properties are obtained.

6           Prior art polymers have suffered from one or more  
7    difficulties affecting their physical properties. The difficulties  
8    include broadened molecular weight distributions, broadened  
9    composition distribution of comonomer, and inefficient distribution or  
10   dispersion of the comonomer along the polyethylene chain of the  
11   copolymer.

12           Broadened molecular weight distribution of a polymer strongly  
13   influences its melt flow properties and such polymers tend to have a  
14   high concentration of high molecular weight molecules making them  
15   subject to orientation. As a result, such resins produce strongly  
16   anisotropic physical properties in the machine versus transverse  
17   direction of a fabrication process and such properties are detrimental  
18   to a number of end use applications.

19           Broad molecular weight distribution resins also frequently  
20   contain a significant portion of quite low molecular weight material.  
21   These molecules almost invariably contain high concentrations of  
22   comonomer and therefore tend to be amorphous or of a low degree of  
23   crystallinity. Consequently, these materials exude to the surface of  
24   fabricated parts causing tackiness where not desired and/or interfere  
25   with other additives in the polymer designed according to the  
26   particular application. An example of this is the surface active  
27   property associated with slip agents in blown or cast film.

28           Most prior art copolymers tend to have a very broad  
29   composition distribution of comonomer, i.e., the distribution of  
30   comonomer among the polymer molecules being nonuniform, some molecules  
31   having a relatively high concentration of comonomer while others have  
32   a relatively low concentration of comonomer. This structural property  
33   of the prior art polymers allows that portion with low comonomer  
34   content to have a high melting point and vice versa leading to a broad  
35   melting range for the entire polymer composition. Of course the  
36   presence of a high melting component is disadvantageous for many  
37   applications where softness is desired and may lead to undesired

1 stiffness. On the other hand, the presence of high comonomer content  
2 materials of low melting point frequently results in a high quantity  
3 of extractables.

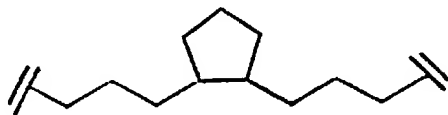
4 Prior art materials are generally characterized by relatively  
5 inefficient use of comonomer moieties along the polyethylene chains.  
6 The distribution of the comonomer along the chain is very important in  
7 determining the efficiency of use of the comonomer and the resulting  
8 properties of the polymer, especially with respect to  
9 crystallizability of the polymer. Such prior art polymers tend to  
10 have a high degree of clustering of the comonomer moieties along the  
11 polyethylene chain. That is, the comonomer units are adjacent or  
12 nonisolated along the chain resulting in inefficient use of the  
13 comonomer since only a single polyethylene chain interruption results  
14 when several comonomer units are contiguous. This has extremely  
15 important implications in the total amount of comonomer required to  
16 achieve the desired crystallinity. Also, it is often disadvantageous  
17 to include unneeded portions of comonomer, especially when dealing  
18 with less available and more expensive diene comonomers. Frequently,  
19 the requirement to use a higher portion of comonomer also tends to  
20 force the comonomer into low molecular weight, high comonomer content  
21 ends of the molecular weight distribution. Accordingly, improved  
22 ethylene copolymers, terpolymers, and interpolymers in the entire  
23 range of amorphous to highly crystalline polymers is needed.

24 Even though recognized as desirable to incorporate a  
25 significant percentage of diene into an ethylene copolymer, catalyst  
26 systems which produce such polymers with narrow molecular weight  
27 distribution and/or narrow comonomer distribution are ineffective in  
28 incorporating dienes in any significant amount.

#### 29 Summary of the Invention

30 The present invention is directed to new ethylene copolymers,  
31 especially ethylene/1,3-butadiene copolymers, especially those having  
32 a concentration of cyclopentane structures as

1 disruptions in the polyethylene backbone. The present invention is  
2 new ethylene copolymers having cyclopentane rings in the ethylene  
3 chain, connected in the 1 and 2 positions on the ring.



4 In accordance with the present invention, a new metallocene/  
5 alumoxane catalyst is provided for olefin polymerization which  
6 catalyst can be usefully employed for the production of low, medium  
7 and high density polyethylenes and copolymers of ethylene with  
8 alpha-olefins having 3 to 18 or more carbon atoms and/or diolefins  
9 having up to 18 carbon atoms or more.

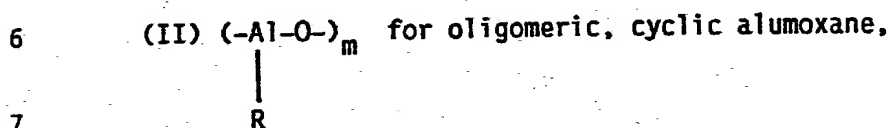
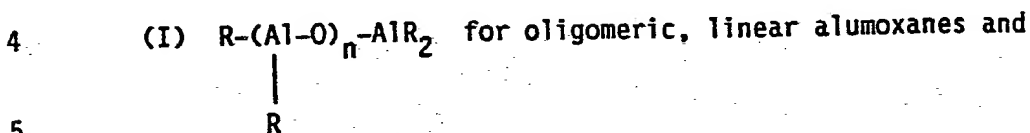
10 The new catalyst provided in accordance with one embodiment  
11 of this invention, comprises the reaction product of at least one  
12 metallocene and an alumoxane in the presence of an support material  
13 thereby providing a supported metallocene-alumoxane reaction product  
14 as the sole catalyst component.

15 The supported reaction product will polymerize olefins at  
16 commercially respectable rates without the presence of the  
17 objectionable excess of alumoxane as required in the homogenous  
18 system.

19 In yet another embodiment of this invention there is  
20 provided a process for the polymerization of ethylene and other  
21 olefins, and particularly homopolymers of ethylene and copolymers of  
22 ethylene and higher alpha-olefins and/or diolefins and/or cyclic  
23 olefins such as norbornene in the presence of the new catalysts.

24 The metallocenes employed in the production of the reaction  
25 product on the support are organometallic coordination compounds  
26 which are cyclopentadienyl derivatives of a Group 4b, 5b, or 6b metal  
27 of the Periodic Table (56th Edition of Handbook of Chemistry and  
28 Physics, CRC Press [1975]) and include mono, di and  
29 tricyclopentadienyls and their derivatives of the transition metals.  
30 Particularly desirable are the metallocene of a Group 4b and 5b metal  
31 such as titanium, zirconium, hafnium and vanadium. The alumoxanes  
32 employed in forming the reaction product with the metallocenes are  
33 themselves the reaction products of an aluminum trialkyl with water.

1           The alumoxanes are well known in the art and comprise  
2 oligomeric linear and/or cyclic alkyl alumoxanes represented by the  
3 formula:



10 wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R  
11 is a  $C_1-C_8$  alkyl group and preferably methyl. Generally, in the  
12 preparation of alumoxanes from, for example, aluminum trimethyl and  
13 water, a mixture of linear and cyclic compounds is obtained.

14           The alumoxanes can be prepared in a variety of ways.  
15 Preferably, they are prepared by contacting water with a solution of  
16 aluminum trialkyl, such as, for example, aluminum trimethyl, in a  
17 suitable organic solvent such as benzene or an aliphatic hydrocarbon.  
18 For example, the aluminum alkyl is treated with water in the form of a  
19 moist solvent. In a preferred method, the aluminum alkyl, such as  
20 aluminum trimethyl, can be desirably contacted with a hydrated salt  
21 such as hydrated ferrous sulfate. The method comprises treating a  
22 dilute solution of aluminum trimethyl in, for example, toluene with  
23 ferrous sulfate heptahydrate.

#### 24 Brief Description of the Drawings:

25           Figure 1 is a graphic and verbal depiction of the concept of  
26 cluster index;

27           Figure 2 is a plot of cluster index against mole percent  
28 comonomer for several commercial resins and the resins of the  
29 invention;

30           Figure 3 is a overlay plot of the molecular weight  
31 distribution of the resins of the invention over that for commercial  
32 resin 3, plotted against weight percent comonomer content;

            Figure 4 is a plot of compositional distribution of comonomer  
in weight percent versus elution temperature for a resin of the

1 invention and several commercial resins;

2 Figure 5 is a plot evidencing the correlation of elution  
3 temperature against composition in mole percent comonomer (branches/  
4 1000 carbon atoms;

5 Figure 6 is a plot of melting point DSC for the copolymer of  
6 the invention and some commercial polymers, showing the relative  
7 narrowness of the invention resin melting point.

8 Description of the Preferred Embodiments:

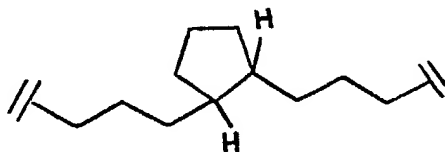
9 A preferred embodiment of the present invention is a  
10 copolymer from the polymerization of ethylene and at least one other  
11 polymerizable comonomer comprising 1,3-butadiene, said copolymer  
12 incorporating in its structure at least about 3 mol percent of said at  
13 least one polymerizable comonomer and having a cluster index of about  
14 9 or less.

15 A preferred embodiment of the present invention is a  
16 copolymer composition of ethylene and butadiene, said copolymer having  
17 a molecular weight distribution ( $M_w/M_n$ ) of about 3.0 or less.

18 A preferred embodiment of the present invention is a method  
19 for preparing copolymers of ethylene and butadiene comprising carrying  
20 out the polymerization in the presence of a metallocene/alumoxane  
21 catalyst system and forming an uncross-linked ethylene/butadiene  
22 copolymer composition.

23 A preferred embodiment of the present invention is an  
24 copolymer from the polymerization of ethylene and at least one other  
25 polymerizable comonomer comprising butadiene, said copolymer having a  
26 composition distribution wherein at least about 55 weight percent of  
27 the copolymer molecules have a comonomer content within 50% of the  
28 median comonomer content in mole percent, of said copolymer.

29 A preferred embodiment of the present invention is an  
30 ethylene copolymer comprising in its polyethylene chain trans  
31 1,2-cyclopentanes.



1           A preferred embodiment of the present invention is an  
2 ethylene copolymer comprising in its polyethylene chain, as the only  
3 cyclopentane unit, trans 1,2-cyclopentane.

4           The term copolymer is intended to include co-, ter-, and  
5 higher interpolymers of ethylene, 1,3-butadiene; and optionally other  
6 polymerizable comonomers. The copolymers have, in the ethylene  
7 backbone, a plurality of cyclopentane rings connected at adjacent  
8 carbons (1,2-).

9           The copolymers of the invention preferably have at least  
10 about 10 percent, more preferably at least about 50 percent of the  
11 butadiene incorporated in the form of the cyclopentane rings.

12           The copolymers of the invention may also include  
13 incorporation of butadiene in the linear 1,4 (cis and trans)  
14 configuration as well as the well-known 1,2 configuration (vinyl  
15 branch on the chain backbone).

16           In a preferred embodiment the copolymers are predominantly  
17 (50-100%) cyclopentane incorporation and the remainder (0-50%) 1,4 or  
18 1,2 incorporation. The 1,4 incorporation is usually greater than the  
19 1,2 incorporation of butadiene in the polymers of the invention.

20           The use of butadiene in copolymerizing (or terpolymerizing or  
21 higher) ethylene tends to produce polymers of higher molecular weight  
22 compared to comparable processes with an alpha olefin.

23           According to the invention the butadiene is incorporated in  
24 the copolymer (or higher polymer) with two adjacent carbon atoms of a  
25 cyclopentane ring in the backbone (no unsaturation). Some of the  
26 butadiene incorporates in the trans 1,4 configuration forming a  
27 straight backbone with one unsaturation. Some of the butadiene may  
28 also incorporate into the copolymer in the cis 1,4 configuration also  
29 forming a straight backbone with one unsaturation (C = C double bond)  
30 but having both of the hydrogens associated with the double bond  
31 carbons on the same side of the double bond. Finally, some of the  
32 butadiene, usually a very small to nil portion, may incorporate in the  
33 1,2 configuration leaving a pendant vinyl group as an unsaturated  
34 branch on the saturated carbon chain. Therefore the copolymer can be  
35 formed with a sufficient amount of residual unsaturation in the  
36 backbone or in side chains for eventual use in special applications  
37 such as crosslinking or chemical modification.

1           The ethylene copolymers of the invention have improved  
2 properties resulting especially from the more efficient use of diene  
3 comonomer in controlling the crystallizability of the polymer. That  
4 is, the efficient use of the diene comonomer comprises an improved  
5 isolation of the comonomer molecules along the polyethylene chain as  
6 not previously achieved for such ethylene copolymers. Accordingly,  
7 the polymers of the present invention not only have especially good  
8 application for those uses previously employing such polymers, but  
9 also have excellent overall physical properties marking a significant  
10 improvement over those materials previously available. The improved  
11 properties of the invention result from the isolated dispersion of the  
12 diene comonomer and other comonomers along the sequence of the polymer  
13 molecule of the invention.

14           Another preferred embodiment copolymer of the present  
15 invention has a distribution wherein more than 55 weight percent of  
16 the copolymer molecules are within 50 percent of the median comonomer  
17 content in mole percent, said copolymer being formed by polymerization  
18 in the presence of a catalyst system comprising a metallocene of a  
19 metal of Group IVB, VB, and VIB of the Periodic Table and an alumoxane  
20 or reaction product thereof.

21           The copolymer products of the present invention comprise  
22 batchwise or continuously produced bulk polymer compositions having  
23 the properties and characteristics described herein. No such  
24 compositions have heretofore been discovered. That is, the  
25 entire/unmodified polymerization product has the advantageous  
26 properties.

27           The copolymer compositions of the invention may be prepared  
28 from the polymerization of ethylene and at least one comonomer. The  
29 at least one comonomer comprises, that is always includes some (or  
30 all) of the 1,3-butadiene.

31           The 1,3-butadiene comonomers incorporated in the polymers of  
32 the invention may be in small or large quantity relative to the amount  
33 of ethylene in the polymer. In one embodiment of the invention, the  
34 polymers of the invention contain at least a minimum of about 3 mole  
35 percent total comonomer based on the moles of ethylene and comonomers,  
36 so as to provide wide dispersion of the comonomers in the polymer  
37 product composition. This generally limits the density to a number

1 below .930 g/cc, preferably below 0.92 g/cc depending on the  
2 copolymers chosen and the method of incorporation. Thus, where only a  
3 two component polymer composition is formed from ethylene and the  
4 diene, at least about 3 mole percent diene units and no more than  
5 about 97 mole percent ethylene units are present. For terpolymers and  
6 higher interpolymers of the invention, only about 0.01 mole percent or  
7 more, preferably about 0.1 mole percent or more, more preferably 1  
8 mole percent or more of the diene need be incorporated so long as the  
9 total incorporation of comonomers [diene and other(s)] is at least  
10 about 3 mole percent for this embodiment.

11 Despite incorporation of at least about 3 mole percent  
12 comonomer units in one embodiment of the polymer compositions of the  
13 invention the polymers nevertheless have a low cluster index and  
14 preferably other characteristics described herein. The total  
15 comonomer content of the polymers of the invention may be the  
16 predominant portion of the polymer. Preferably, especially for solid  
17 polymers, the ethylene units are the predominant component on a molar  
18 basis.

19 In one preferred embodiment of the present invention the  
20 polymers of the invention have improved properties attributable to the  
21 more uniform content of diene and other comonomers among the polymer  
22 molecules.

23 In contrast to the prior art polymers, the copolymers,  
24 terpolymers, and other interpolymers of the present invention exhibit  
25 very little clustering of the comonomer molecules along the  
26 polyethylene chain both with respect to the diene comonomer and any  
27 other polymerizable comonomer formed in the polyethylene chain. As a  
28 result, the use of comonomers in forming the copolymers of the  
29 invention is very efficient in controlling crystallizability, wards  
30 against formation of high comonomer content/low molecular weight ends,  
31 reduces cost, and improves properties.

32 In a preferred embodiment of the present invention, the  
33 copolymers of the invention have very narrow composition distribution  
34 of comonomer. That is, the copolymers have much more uniform  
35 distribution of comonomer among the molecules thereby largely avoiding  
36 the problem presented by broad composition distribution resins.

1           In another preferred delineation of the invention, the  
2 copolymers of the invention have improved properties resulting from  
3 the more consistent size of polymer molecules not achieved in the  
4 prior art. This aspect of the more preferred embodiment is generally  
5 referred to as a lower molecular weight distribution or ratio of the  
6 weight average molecular weight to number average molecular weight of  
7 the polymer material.

8           Also in this preferred embodiment of the present invention,  
9 the copolymers of the invention exhibit relatively narrow molecular  
10 weight distribution. That is, they have a relatively low ratio of  
11 weight to number average molecular weight. In other words, the  
12 concentration of very high molecular weight molecules and very low  
13 molecular weight molecules is decreased over prior art polymers. The  
14 absence of the high molecular weight molecules reduces the tendency  
15 for orientation in fabrication processes and increases isotropic  
16 machine/transverse direction physical properties. The absence of low  
17 molecular weight molecules (low tail) in the copolymers of the  
18 invention reduces the tendency to form tacky surfaces and otherwise  
19 interfere with surface active agents in certain applications of the  
20 copolymers of the present invention.

21           Polymers of the prior art do not have the structure and  
22 corresponding properties of the polymers of the invention. That is,  
23 they lack the low cluster index for ethylene copolymers (including  
24 terpolymers and higher interpolymers) having therein at least about 3  
25 mole percent, preferably 5 mole percent, more preferably 10 mole  
26 percent comonomer units according to the invention. The absence of  
27 such structure is generally reflected in easily measured  
28 characteristics of the invention such as melting point temperature  
29 and the like. The prior art polymers also generally lack narrow  
30 molecular weight distribution and narrow comonomer distribution.

31           The polymers of the present invention are capable of being  
32 fabricated into a wide variety of articles, as is known for  
33 homopolymers of ethylene and copolymers of ethylene and higher  
34 alpha-olefins.

35           The polymers of the invention may vary in density in a broad  
36 range from essentially amorphous materials to highly crystalline  
37 materials. They may be liquids (such as for certain rubbers and

1 lubricants and waxes) or solids.

2 The molecular weight of the copolymers of the invention may  
3 vary over a broad range. Preferably the polymers have a number  
4 average molecular weight of about 500 or higher, preferably 1000 or  
5 higher, more preferably about 10,000 or higher. Typically, materials  
6 used for elastomers applications are either copolymers or terpolymers  
7 (often with propylene monomer) in the density range of about  
8 0.86-0.87 g/cc. Typically, these polymers contain 30 weight percent  
9 or more of the comonomers and the balance ethylene. Frequently, the  
10 elastomers of the unsaturated polymers of the invention will have as  
11 much as 48 weight percent of the comonomer present.

12 The polymers of the present invention may also include  
13 plastomers in the density range of about 0.87-0.900 g/cc and  
14 containing from about 20-30 weight percent of comonomer. Also  
15 available in the polymers of the invention are the very low density  
16 polyethylene materials of density range 0.900-0.915 g/cc and having  
17 from about 10-20 weight percent comonomer present.

18 The polymers of the invention may be formed as a linear low  
19 density polyethylene type polymer in the density range of about 0.915  
20 g/cc to about 0.940 g/cc and containing from about 5-10 weight  
21 percent of the comonomers. The polymers of the invention may also be  
22 used in the form of high density polyethylene having a density of  
23 about 0.940 g/cc and above and containing up to about 5 weight  
24 percent comonomers. The unsaturated polymers of the invention may  
25 also form amorphous materials below a density of 0.86 g/cc including  
26 tackifier resins.

27 The polymers of the present invention have particularly  
28 advantageous properties because of their narrow molecular weight  
29 distribution, narrow compositional distribution, and their chain  
30 configuration having isolated comonomer units.

31 Sequence distributions, or the distribution of comonomer  
32 units along a polymer chain, in, e.g., linear low density  
33 polyethylenes is a factor affecting the cost of the polymer because  
34 it affects the amount of comonomer required to achieve a desired  
35 polymer density. If comonomer is efficiently incorporated, i.e.,  
36 with little clustering of comonomer units, in a linear low density  
37 polyethylene, less comonomer is required to depress the density.

1 Thus, the number of comonomer runs in a copolymer chain and the  
2 length of each run is significant in the structure of the  
3 polyethylene molecules and affects the physical properties of the  
4 polymer. The polymers of the present invention are marked by a  
5 relatively high number of single units of comonomer in the polymer  
6 chain relative to the number of units containing more than a single  
7 comonomer molecule in comparison to unsaturated polymers of the prior  
8 art.

9 The ethylene polymers of the invention are hereinafter  
10 described by their "cluster index". This index reflects the degree  
11 to which the polymers of the invention have individual comonomer  
12 units dispersed along the polyethylene chain, preferably in favoring  
13 isolation of individual units over groups of two or more units.  
14 Given a minimum level of comonomer, the unsaturated ethylene polymers  
15 of the present invention are especially noted for their efficient use  
16 of comonomer molecules by having more isolated comonomer molecules  
17 along the polyethylene chain and fewer clusters of molecules of the  
18 comonomer in the polyethylene chain. That is, the unsaturated  
19 polymers of the present invention tend to deviate from random  
20 comonomer distribution in the direction of fewer contiguous comonomer  
21 sequences. Thus, the cluster index permits a quantitative evaluation  
22 of the deviation from a random distribution of comonomer in the  
23 polymer chain.

24 In the cluster index description given herein, there are two  
25 reference points. The reference point 0 describes a polymer which  
26 has only isolated comonomer insertions without any contiguous  
27 comonomer units in a cluster; of course this describes pure  
28 homopolymers also. The second reference point is the number 10  
29 describing an ethylene copolymer having comonomer distribution that  
30 is exactly random (Bernoullian) and thus containing a predictable  
31 amount of contiguous comonomer units. Any polymer having a cluster  
32 index value greater than 10 contains proportionally more contiguous  
33 comonomer sequences than predicted by the random distribution. Any  
34 polymer having a cluster index value between 0 and 10 is indicated to  
35 have fewer contiguous sequences than a random distribution polymer  
36 (given a minimum of comonomer). These values are typically  
37 associated with the method of producing the polymer including the

1 catalyst used and conditions of polymerization.

2 The cluster index comparisons are best made for polymers  
3 having comparable comonomer mole contents or densities. The  
4 measurement of the clustering of the comonomer along the polyethylene  
5 chain in a given polymer may be determined by a study using carbon 13  
6 nuclear magnetic resonance spectroscopy ( $C^{13}$ NMR). Using this tool  
7 for evaluation, the cluster index may be given as follows:

$$8 \quad \text{Cluster index} = 10 [(X) - (EXE)]/[2(X)^2 - (X)^3]$$

9 where (X) is the mole percent of total comonomer molecules in the  
10 copolymer and EXE is the mole fraction of the triad segment of 3  
11 monomer units containing ethylene-comonomer-ethylene. These  
12 concentrations are easily measured using  $C^{13}$ NMR.

13 The basis for the cluster index is further explained and  
14 exemplified below by the following discussion and in reference to  
15 drawing Figure 1.

16 Referring now to drawing Figure 1 the cluster index may be  
17 derived as follows, using the reference point 10 as random clustering  
18 expected in a polymerization and the reference point 0 as that point  
19 for no clustering in a polymer (no units of more than one comonomer  
20 molecule contiguous). Accordingly,

$$21 \quad \text{Cluster index} = 10 - 10 \times \frac{[(EXE)_{\text{observed}} - (EXE)_{\text{random}}]}{[(X) - (EXE)_{\text{random}}]}$$

23 where "X" is the mole percent comonomer in the ethylene copolymer  
24 and EXE is the corresponding triad configuration of a single  
25 comonomer molecule contiguous to two ethylene molecules (units).

26 The term  $(EXE)_{\text{random}}$  serves as a reference point and its  
27 value can be calculated from any suitable statistical model. In this  
28 case the Bernoullian model was chosen. For the Bernoullian model

$$29 \quad (EXE)_{\text{random}} = [1 - X]^2[X].$$

31  
32 Thus, substituting this value of  $(EXE)_{\text{random}}$  in the formula for  
33 cluster index above gives:

$$\text{Cluster index} = 10 [(X) - (EXE)_{\text{observed}}] / [2(X)^2 - (X)^3]$$

Accordingly, it can be readily seen from drawing Figure 1 that those polymers having more comonomer clustering than a random distribution appear to the left of the reference point 10 and those having less comonomer clustering than a random distribution appear between 0 and 10.

In Figure 2, polymers are plotted according to their cluster index as described for Figure 1 and using the vertical axis to plot mole percent of comonomer of the polymer samples. It is readily apparent from drawing Figure 2 that those polymers of the invention have a reduced cluster index (for a given density comonomer content) over polymers of the prior art such as those commercial polymers plotted and appearing near or to the left of reference point 10 (random clustering). The technique of using the  $C^{13}$ NMR to obtain the information for cluster index is known to the skilled artisan.

Also shown for comparison in Figure 2 is the cluster index of Dowlex 2088 octene LLDPE copolymer (Resin 9), Dowlex 2517 octene LLDPE copolymer (Resin 10), and Union Carbide 7099 hexene LLDPE copolymer (Resin 11).

The cluster index improvement in the polymers of the invention versus polymers of the prior art is detectable at 3 mole percent comonomer content, readily discernable at 5 mole percent, and remarkable at about 10 mole percent or higher.

The above described cluster index may be considered to be of the first order or based on the total number of comonomer units less the isolated (EXE) comonomer units. A higher order cluster index can also be measured and calculated as based primarily on the occurrence of dimer segments (EXX) or (XXE) as observed. This measurement is somewhat more discriminating at low comonomer mole percents (about 3). Thus an EXX index may in like fashion be calculated as

$$\text{EXX Index} = 10 - 10 \frac{(\text{EXX})_{\text{observed}} - (\text{EXX})_{\text{Bernoullian}}}{(\text{EXX})_{\text{Bernoullian}}}$$

Since  $(\text{EXX})_{\text{Bernoullian}} = 2 [E] [X]^2$  and the (EXX) observed is based on both (EXX) and (XXE) units, readily measured by

1  $C^{13}$  NMR, the EXX index is readily achieved. For such index a  
2 totally random polymer is measured as 10, a totally dimerless polymer  
3 is 0 (no contiguous XX), and a polymer increasingly deficient in  
4 solitary units (EXE) will approach 20.

5 The EXX index is a second measure of polymer structure based  
6 directly on dimers and higher orders of contiguous (EXX and XEX)  
7 observed; it may be used independently or together with the cluster  
8 index (EXE) to distinguish polymers.

9 The EXX index for commercial resins 3, 5 and 6 listed in the  
10 Table herein are 7.3, 12.4, and 15.0.

11 The ethylene polymers of the present invention are  
12 preferably marked by a relatively narrow molecular weight  
13 distribution in comparison to prior art polymers. The molecular  
14 weights and molecular weight distributions were determined using  
15 Waters 150C Gel Permeation Chromatographic Instruments. These  
16 instruments were equipped with refractive index detectors operated at  
17 145°C and at a solvent flow rate of 1 milliliter per minute. The  
18 solvent used was ultra-high purity grade 1,2,4-trichlorobenzene  
19 obtained from Burdick and Jackson Company. Prior to use, the solvent  
20 was filtered through a 0.5 micron filter and stabilized with 120 ppm  
21 BHT. Three Waters styragel columns were used with nominal porosities  
22 of 500, 10,000, and 1,000,000 angstroms. Each polymer sample was  
23 dissolved in trichlorobenzene solvent at 145°C to a concentration  
24 level of about 0.1 weight percent and thereafter filtered through a  
25 0.5 micron porous metal filter. About 300 microliters of this  
26 solution was then injected into the gel permeation chromatograph.  
27 Analysis time was typically 45 minutes. Calibration of the  
28 instrument for molecular weight determination was accomplished with  
29 the use of narrow molecular weight distribution polystyrene standards  
30 obtained from Toyo Soda Manufacturing Company. Sixteen of the  
31 standards were used ranging in molecular weight from 526 - 5.2 x  
32  $10^6$ . Molecular weight distributions of these standards were listed  
33 at 1.0-1.15 as measured by the ratio of weight average molecular  
34 weight to number average molecular weight. These polystyrene  
35 molecular weight data were then converted to a polyethylene basis  
36 with the use of the Mark-Houwink equation and the use of the  
37 following constants:

1                   for polyethylene  $K = 5.17 \times 10^{-4}$ ,  $a = 0.70$   
2                   for polystyrene  $K = 2.78 \times 10^{-4}$ ,  $a = 0.70$ .

3   Each sample was run twice and the calculated results averaged to  
4   yield the molecular weight information reported. The molecular  
5   weight distribution of the resin of Example 1 below was plotted for  
6   comparison on the same plot with that for Exxon LL3001 linear low  
7   density polyethylene resin mole percent comonomer on a scale of the  
8   log of molecular weight versus weight percent of the polymer in the  
9   molecular weight range. As can be seen from drawing Figure 3 the  
10   polymer of the invention has a strictly narrower molecular weight  
11   distribution than the commercially available linear low density  
12   polyethylene.

13                The polymers of the present invention preferably also have a  
14   narrow distribution of comonomer amongst molecules of the polymer in  
15   comparison to prior art polymers. For comparison, drawing Figure 4  
16   reflects the narrow distribution of the unsaturated polymer of  
17   Example 1 in comparison to the relatively broad comonomer  
18   distribution polymers of the prior art. In Figure 4 the weight  
19   percent of copolymer (having a given comonomer content) is plotted  
20   against an elution temperature which directly reflects comonomer  
21   content. A better understanding of this preferred embodiment of the  
22   polymers of the present invention will be had by a review of Figure 4  
23   and the following discussion.

24                Crystalline copolymers may be fractionated by comonomer  
25   content over a temperature range from 0-120°C in tetrachloroethylene  
26   solvent. The compositions of the fractions of the solution are  
27   determined and a solution temperature versus composition calibration  
28   curve has been constructed based on the data obtained. Using this  
29   calibration curve, the temperature scale of the solubility  
30   distribution curve can be converted to a composition scale and a  
31   composition distribution curve is thus obtained as in drawing Figure  
32   4.

33                A machine has been assembled to automatically determine the  
34   solubility distribution curve of a crystalline copolymer. In the  
35   measuring instrument, a steel column is packed with small mesh glass  
36   beads and immersed in an oil bath whose temperature can be programmed  
37   over a temperature range from about 0°C-150°C. The

1 tetrachloroethylene solvent may be prevented from boiling by  
2 operating the instrument at about 3 atmospheres pressure under an  
3 automatic regulator. A weighed amount of sample, usually about 1.6  
4 grams, is placed in a sample preparation chamber, sealed, and  
5 repeatedly evacuated and filled with argon. A metered volume of  
6 solvent is then pumped into the sample preparation chamber where it  
7 is stirred and heated to obtain a solution of about 1 percent  
8 concentration. A metered volume of this solution, usually about  
9 100 cc is then pumped into the packed column which has been  
10 thermostated at a high temperature of usually at least about 120°C.

11 The polymer solution sample is subsequently crystallized by  
12 cooling the polymer in the column to 0°C at a programmed rate of 5°C  
13 per hour. The column was then maintained at 0°C for at least an  
14 hour. Thereafter, the elution stage of the determination is started  
15 by pumping pure solvent through the column at a rate of 6 cc per  
16 minute. Effluent from the column passes through the reheater where  
17 it is heated to 120°C before passing through an IR detector used to  
18 measure the absorbance of the effluent stream. The infrared  
19 absorption of the polymer carbon hydrogen stretching bands at about  
20 2960 centimeter<sup>-1</sup> serves as a continuous measure of the relative  
21 concentration of polymer in the effluent. After passing through the  
22 infrared detector the temperature of the effluent is reduced to about  
23 110°C and the pressure is reduced to 1 atmosphere before passing the  
24 stream into an automatic fraction collector. In the elution stage,  
25 the pure solvent is pumped through the column set at 0°C for one  
26 hour. This serves to flush polymer that has not crystallized during  
27 the crystallization stage out of the column so that the relative  
28 percent of uncrystallized polymer can be determined from the infrared  
29 trace. The temperature is then programmed upward at 10°C per hour to  
30 100°C and at 20°C per hour from 100°C to 120°C.

31 The compositions of fractions obtained from the various  
32 polymers were determined by infrared spectroscopy. The IR  
33 compositions are obtained from the intensity of the 1378cm<sup>-1</sup> methyl  
34 band, the thickness of the sample, and a calibration curve based on  
35 samples whose compositions were determined independently by  
36 C<sup>13</sup>NMR. No corrections for methyl polymer end groups was made in  
37 obtaining compositions from infrared data.

1           Figure 5 is a plot of the elution temperature versus the  
2 comonomer content in mole percent comonomer (branches per 1000 carbon  
3 atoms) for the fractions of the sample. The curve "A" has been drawn  
4 through the points. Thus, curve A may be used as a correlation  
5 between elution temperature and composition of the polymer for  
6 temperatures greater than 0°C. The calibration curve is most  
7 accurate for fractions with number average molecular weights,  $M_n$   
8  $\geq 10,000$  as determined by size exclusion chromatography.

9           As seen in drawing Figure 4, samples of polymers tend to  
10 have a peak at about 0°C elution temperature. This small peak  
11 represents the fraction of total polymer that is not crystallizable  
12 at the lowest temperature of the experiment (about 0°C).

13           In summary, the device and procedure described provide a  
14 plot of relative weight percent of polymer versus elution temperature  
15 which in turn may be correlated to composition and mole percent  
16 comonomer (branches per 1000 carbon atoms) in the polymer chain.  
17 Accordingly, drawing Figure 4 is an effective comparison of the  
18 comonomer distribution of the polymers of the invention to that for  
19 certain commercial polymers. As can readily be seen, the composition  
20 distribution of the polymer of the invention example is quite narrow  
21 in comparison.

22           In forming the polymers of the present invention it may be  
23 necessary to purify, or isolate the diene and other, optional  
24 comonomers of the invention in order to obtain incorporation thereof  
25 during polymerization. One such recommended technique is passing the  
26 comonomer, especially the diene, over alumina to remove extraneous  
27 materials.

28           Figure 6 shows the melting point by differential scanning  
29 calorimetry (DSC) results for the resins of the invention in  
30 comparison to some commercial resins. Melting point distributions  
31 were determined using a Perkin Elmer DSC-7 operated in the following  
32 fashion: About 5-6 mg of sample was heated to 160°C and held at that  
33 temperature for 5 minutes. The sample was then cooled at 10°C per  
34 minute to a temperature of 0°C and reheated at 10°C per minute. The  
35 melting distributions reported here were collected during this  
36 reheating at 10°C per minute.

1           Concentrations of unsaturation in ethylene based polymers  
2 was determined by comparisons of IR spectra of brominated versus  
3 original polymer specimens utilizing the following bands:

4           vinylene       - 965  $\text{cm}^{-1}$   
5           vinyl         - 909  $\text{cm}^{-1}$   
6           vinylidene   - 888  $\text{cm}^{-1}$

7           Various analyses of the copolymers of the invention and  
8 polymers formed by the method of the invention disclose that such  
9 copolymers have a significant predominance of ring addition of the  
10 butadiene versus 1,2 addition which can lead to long chain branching  
11 and/or intermolecular coupling. A predominance of 1,2 addition can  
12 in fact lead to crosslinking of the copolymer as found in the prior  
13 art. All of the polymers of the present invention are essentially  
14 entirely uncrosslinked, non-gel materials.

15           The degree of intermolecular coupling and/or long chain  
16 branching of the polymers of the invention may vary from a copolymer  
17 composition which is substantially devoid of such branching and  
18 coupling and which behaves rheologically as linear molecules to the  
19 composition which has a high degree of long chain branching and  
20 intermolecular coupling without being crosslinked. The polymers are  
21 generally not a crosslinked product and are soluble in refluxing  
22 xylene in accordance with recognized methods. That is, substantially  
23 all of, usually greater than 98% of, the copolymers of the invention  
24 are soluble in refluxing xylene.

25           A better understanding of the present invention will be had  
26 by a review of the following examples taken in conjunction with the  
27 drawing figures. The best mode of the invention is described herein.

28           Briefly, the transition metal containing catalyst of the  
29 present invention is obtained by reacting an alumoxane and a  
30 metallocene in the presence of a solid support material. The  
31 supported reaction product can be employed as the sole catalyst  
32 component for the polymerization of olefins or, in the alternative,  
33 it can be employed with a organometallic cocatalyst.

34           Typically, the support can be any of the solid,  
35 particularly, porous supports such as talc, inorganic oxides, and  
36 resinous support materials such as polyolefin. Preferably, the  
37 support material is an inorganic oxide in finely divided form.

1           Suitable inorganic oxide materials which are desirably  
2 employed in accordance with this invention include Group 2a, 3a, 4a  
3 or 4b metal oxides such as silica, alumina, and silica-alumina and  
4 mixtures thereof. Other inorganic oxides that may be employed either  
5 alone or in combination with the silica, alumina or silica-alumina  
6 are magnesia, titania, zirconia, and the like. Other suitable  
7 support materials, however, can be employed, for example, finely  
8 divided polyolefins such as finely divided polyethylene.

9           The metal oxides generally contain acidic surface hydroxyl  
10 groups which will react with the alumoxane or transition metal  
11 compound first added to the reaction solvent. Prior to use, the  
12 inorganic oxide support is dehydrated, i. e., subjected to a thermal  
13 treatment in order to remove water and reduce the concentration of  
14 the surface hydroxyl groups. The treatment is carried out in vacuum  
15 or while purging with a dry inert gas such as nitrogen at a  
16 temperature of about 100°C to about 1000°C, and preferably, from  
17 about 300°C to about 800°C. Pressure considerations are not  
18 critical. The duration of the thermal treatment can be from about 1  
19 to about 24 hours. However, shorter or longer times can be employed  
20 provided equilibrium is established with the surface hydroxyl  
21 groups.

22           Chemical dehydration as an alternative method of dehydration  
23 of the metal oxide support material can advantageously be employed.  
24 Chemical dehydration converts all water and hydroxyl groups on the  
25 oxide surface to inert species. Useful chemical agents are for  
26 example,  $\text{SiCl}_4$ ; chlorosilanes, such as trimethylchlorosilane,  
27 dimethylaminotrimethylsilane and the like. The chemical dehydration  
28 is accomplished by slurring the inorganic particulate material, such  
29 as, for example, silica in an inert low boiling hydrocarbon, such as,  
30 for example, hexane. During the chemical dehydration reaction, the  
31 silica should be maintained in a moisture and oxygen-free  
32 atmosphere. To the silica slurry is then added a low boiling inert  
33 hydrocarbon solution of the chemical dehydrating agent, such as, for  
34 example, dichlorodimethylsilane. The solution is added slowly to the  
35 slurry. The temperature ranges during chemical dehydration reaction  
36 can be from about 25°C to about 120°C, however, higher and lower  
37 temperatures can be employed. Preferably, the temperature will be

1     about 50°C to about 70°C. The chemical dehydration procedure should  
2     be allowed to proceed until all the moisture is removed from the  
3     particulate support material, as indicated by cessation of gas  
4     evolution. Normally, the chemical dehydration reaction will be  
5     allowed to proceed from about 30 minutes to about 16 hours,  
6     preferably 1 to 5 hours. Upon completion of the chemical  
7     dehydration, the solid particulate material is filtered under a  
8     nitrogen atmosphere and washed one or more times with a dry,  
9     oxygen-free inert hydrocarbon solvent. The wash solvents, as well as  
10    the diluents employed to form the slurry and the solution of chemical  
11    dehydrating agent, can be any suitable inert hydrocarbon.  
12    Illustrative of such hydrocarbons are heptane, hexane, toluene,  
13    isopentane and the like.

14           The normally hydrocarbon soluble metallocenes and alumoxanes  
15    are converted to a heterogeneous supported catalyst by depositing  
16    said metallocenes and alumoxanes on the dehydrated support material.  
17    The order of addition of the metallocene and alumoxane to the support  
18    material can vary. For example, the metallocene (neat or dissolved  
19    in a suitable hydrocarbon solvent) can be first added to the support  
20    material followed by the addition of the alumoxane; the alumoxane and  
21    metallocene can be added to the support material simultaneously; the  
22    alumoxane can be first added to the support material followed by the  
23    addition of the metallocene. In accordance with the preferred  
24    embodiment of this invention the alumoxane dissolved in a suitable  
25    inert hydrocarbon solvent is added to the support material slurried  
26    in the same or other suitable hydrocarbon liquid and thereafter the  
27    metallocene is added to the slurry.

28           The treatment of the support material, as mentioned above,  
29    is conducted in an inert solvent. The same inert solvent or a  
30    different inert solvent is also employed to dissolve the metallocenes  
31    and alumoxanes. Preferred solvents include mineral oils and the  
32    various hydrocarbons which are liquid at reaction temperatures and in  
33    which the individual ingredients are soluble. Illustrative examples  
34    of useful solvents include the alkanes such as pentane, iso-pentane,  
35    hexane, heptane, octane and nonane; cycloalkanes such as cyclopentane  
36    and cyclohexane; and aromatics such as benzene, toluene, ethylbenzene  
37    and diethylbenzene. Preferably the support material is slurried in

1 toluene and the metallocene and alumoxane are dissolved in toluene  
2 prior to addition to the support material. The amount of solvent to  
3 be employed is not critical. Nevertheless, the amount should be  
4 employed so as to provide adequate heat transfer away from the  
5 catalyst components during reaction and to permit good mixing.

6 The supported catalyst of this invention is prepared by  
7 simply adding the reactants in the suitable solvent and preferably  
8 toluene to the support material slurry, preferably silica slurried in  
9 toluene. The ingredients can be added to the reaction vessel rapidly  
10 or slowly. The temperature maintained during the contact of the  
11 reactants can vary widely, such as, for example, from 0° to 100°C.  
12 Greater or lesser temperatures can also be employed. Preferably, the  
13 alumoxanes and metallocenes are added to the silica at room  
14 temperature. The reaction between the alumoxane and the support  
15 material is rapid, however, it is desirable that the alumoxane be  
16 contacted with the support material for about one hour up to eighteen  
17 hours or greater. Preferably, the reaction is maintained for about  
18 one hour. The reaction of the alumoxane, the metallocene and the  
19 support material is evidenced by its exothermic nature and a color  
20 change.

21 At all times, the individual ingredients as well as the  
22 recovered catalyst component are protected from oxygen and moisture.  
23 Therefore, the reactions must be performed in an oxygen and moisture  
24 free atmosphere and recovered in an oxygen and moisture free  
25 atmosphere. Preferably, therefore, the reactions are performed in the  
26 presence of an inert dry gas such as, for example, nitrogen. The  
27 recovered solid catalyst is maintained in a nitrogen atmosphere.

28 Upon completion of the reaction of the metallocene and  
29 alumoxane with the support, the solid material can be recovered by any  
30 well-known technique. For example, the solid material can be  
31 recovered from the liquid by vacuum evaporation or decantation. The  
32 solid is thereafter dried under a stream of pure dry nitrogen or dried  
33 under vacuum.

34 The amount of alumoxane and metallocene usefully employed in  
35 preparation of the solid supported catalyst component can vary over a  
36 wide range. The concentration of the alumoxane added to the  
37 essentially dry, support can be in the range of about 0.1 to about 10

1 mmoles/g of support, however, greater or lesser amounts can be  
2 usefully employed. Preferably, the alumoxane concentration will be in  
3 the range of 0.5 to 10 mmoles/g of support and especially 1 to 5  
4 mmoles/g of support. The amount of metallocene added will be such as  
5 to provide an aluminum to transition metal mole ratio of from about  
6 1:1 to about 100:1. Preferably, the ratio is in the range from about  
7 5:1 to about 50:1 and more preferably in the range from about 10:1 to  
8 about 20:1. These ratios are significantly less than that which is  
9 necessary for the homogeneous system.

10 The unsaturated polymers of the present invention are those  
11 having the narrow cluster index and preferably having the additional  
12 described structure of molecular weight distribution and comonomer  
13 distribution as well as properties herein described. Such polymers  
14 may be prepared by any of the known techniques of polymerization  
15 including solution, high pressure, and gas-phase polymerization  
16 processes.

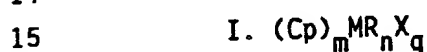
17 The polymers of the invention may be formed by use of  
18 catalyst systems of the metallocene type. That is,  
19 cyclopentadienylide catalyst systems using a metallocene complex in  
20 conjunction with an alumoxane cocatalyst or reaction product thereof  
21 are suitable for preparing polymers of the invention. The metallocene  
22 catalyst may be represented by the general formula  
23  $(C_p)_m M R_n R'_p$  wherein  $C_p$  is a substituted or unsubstituted  
24 cyclopentadienyl ring; M is a Group IVB, VB, or VIB transition metal;  
25 R and R' are independently selected halogen, hydrocarbyl group, or  
26 hydrocarboxyl groups having 1-20 carbon atoms;  $m = 1-3$ ,  $n = 0-3$ ,  $p =$   
27  $0-3$ , and the sum of  $m + n + p$  equals the oxidation state of M.  
28 Various forms of the catalyst system of the metallocene type may be  
29 used for polymerization to achieve polymers of the present invention  
30 including those of the homogeneous or the heterogeneous, supported  
31 catalyst type wherein the catalyst and alumoxane cocatalyst are  
32 together supported or reacted together onto an inert support for  
33 polymerization by gas-phase, high pressure, or solution polymerization.

34 The cyclopentadienyls of the catalyst may be unsubstituted or  
35 substituted with hydrogen or hydrocarbyl radicals. The hydrocarbyl  
36 radicals may include alkyl, alkenyl, aryl, alkylaryl, arylalkyl, and  
37 like radicals containing from about 1-20 carbon atoms or 2 carbon

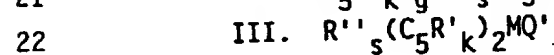
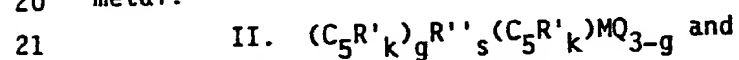
1 atoms joined together to form a  $C_4-C_6$  ring.

2 The present invention employs at least one metallocene  
3 compound in the formation of the supported catalyst. Metallocene,  
4 i.e. a cyclopentadienylide, is a metal derivative of a  
5 cyclopentadiene. The metallocenes usefully employed in accordance  
6 with this invention contain at least one cyclopentadiene ring. The  
7 metal is selected from Group 4b, 5b and 6b metal, preferably 4b and 5b  
8 metals, preferably titanium, zirconium, hafnium, chromium, and  
9 vanadium, and especially titanium and zirconium. The cyclopentadienyl  
10 ring can be unsubstituted or contain substituents such as, for  
11 example, a hydrocarbyl substituent. The metallocene can contain one,  
12 two, or three cyclopentadienyl ring however two rings are preferred.

13 The preferred metallocenes can be represented by the general  
14 formulas:



16 wherein Cp is a cyclopentadienyl ring, M is a Group 4b, 5b, or 6b  
17 transition metal, R is a hydrocarbyl group or hydrocarboxy having from  
18 1 to 20 carbon atoms, X is a halogen, and  $m = 1-3$ ,  $n = 0-3$ ,  $q = 0-3$   
19 and the sum of  $m+n+q$  will be equal to the oxidation state of the  
20 metal.



23 wherein  $(C_5R'_k)$  is a cyclopentadienyl or substituted  
24 cyclopentadienyl, each  $R'$  is the same or different and is hydrogen or  
25 a hydrocarbyl radical such as alkyl, alkenyl, aryl, alkylaryl, or  
26 arylalkyl radical containing from 1 to 20 carbon atoms or two carbon  
27 atoms are joined together to form a  $C_4-C_6$  ring,  $R''$  is a  $C_1-C_4$   
28 alkylene radical, a dialkyl germanium or silicon, or a alkyl phosphine  
29 or amine radical bridging two  $(C_5R'_k)$  rings, Q is a hydrocarbyl  
30 radical such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical  
31 having from 1-20 carbon atoms, hydrocarboxy radical having from 1-20  
32 carbon atoms or halogen and can be the same or different from each  
33 other, Q' is an alkylidene radical having from 1 to about 20 carbon  
34 atoms, s is 0 or 1, g is 0, 1 or 2, s is 0 when g is 0, k is 4 when s  
35 is 1 and k is 5 when s is 0, and M is as defined above.

36 Exemplary hydrocarbyl radicals are methyl, ethyl, propyl,  
37 butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl,

1 cetyl, 2-ethylhexyl, phenyl and the like.

2 Exemplary halogen atoms include chlorine, bromine, fluorine  
3 and iodine and of these halogen atoms, chlorine is preferred.

4 Exemplary hydrocarboxy radicals are methoxy, ethoxy, propoxy,  
5 butoxy, amyloxy and the like.

6 Exemplary of the alkylidene radicals is methyldiene,  
7 ethyldiene and propyldiene.

8 Illustrative, but non-limiting examples of the metallocenes  
9 represented by formula I are dialkyl metallocenes such as  
10 bis(cyclopentadienyl)titanium dimethyl, bis(cyclopentadienyl)titanium  
11 diphenyl, bis(cyclopentadienyl)zirconium dimethyl,  
12 bis(cyclopentadienyl)zirconium diphenyl, bis(cyclopentadienyl)hafnium  
13 dimethyl and diphenyl, bis(cyclopentadienyl)titanium di-neopentyl,  
14 bis(cyclopentadienyl)zirconium di-neopentyl,  
15 bis(cyclopentadienyl)titanium dibenzyl, bis(cyclopentadienyl)zirconium  
16 dibenzyl, bis(cyclopentadienyl)vanadium dimethyl; the mono alkyl  
17 metallocenes such as bis(cyclopentadienyl)titanium methyl chloride,  
18 bis(cyclopentadienyl)titanium ethyl chloride,  
19 bis(cyclopentadienyl)titanium phenyl chloride,  
20 bis(cyclopentadienyl)zirconium methyl chloride,  
21 bis(cyclopentadienyl)zirconium ethyl chloride,  
22 bis(cyclopentadienyl)zirconium phenyl chloride,  
23 bis(cyclopentadienyl)titanium methyl bromide,  
24 bis(cyclopentadienyl)methyl iodide, bis(cyclopentadienyl)titanium  
25 ethyl bromide, bis(cyclopentadienyl)titanium ethyl iodide,  
26 bis(cyclopentadienyl)titanium phenyl bromide,  
27 bis(cyclopentadienyl)titanium phenyl iodide,  
28 bis(cyclopentadienyl)zirconium methyl bromide,  
29 bis(cyclopentadienyl)zirconium methyl iodide,  
30 bis(cyclopentadienyl)zirconium ethyl bromide,  
31 bis(cyclopentadienyl)zirconium ethyl iodide,  
32 bis(cyclopentadienyl)zirconium phenyl bromide,  
33 bis(cyclopentadienyl)zirconium phenyl iodide; the trialkyl  
34 metallocenes such as cyclopentadienyltitanium trimethyl,  
35 cyclopentadienyl zirconium triphenyl, and cyclopentadienyl zirconium  
36 trineopentyl, cyclopentadienylzirconium trimethyl,  
37 cyclopentadienylhafnium triphenyl, cyclopentadienylhafnium

1 trineopentyl, and cyclopentadienylhafnium trimethyl.

2 Illustrative, but non-limiting examples of II and III  
3 metallocenes which can be usefully employed in accordance with this  
4 invention are monocyclopentadienyls titanocenes such as,  
5 pentamethylcyclopentadienyl titanium trichloride,  
6 pentaethylcyclopentadienyl titanium trichloride;  
7 bis(pentamethylcyclopentadienyl) titanium diphenyl, the carbene  
8 represented by the formula bis(cyclopentadienyl)titanium= $\text{CH}_2$  and  
9 derivatives of this reagent such as  
10 bis(cyclopentadienyl) $\text{Ti}-\text{CH}_2-\text{Al}(\text{CH}_3)_3$ ,  $(\text{Cp}_2\text{TiCH}_2)_2$ ,  
11  $\text{Cp}_2\text{TiCH}_2\text{CH}(\text{CH}_3)\text{CH}_2$ ,  $\text{Cp}_2\text{Ti}-\text{CHCH}_2\text{CH}_2$ ; substituted  
12 bis(cyclopentadienyl)titanium (IV) compounds such as:  
13 bis(indenyl)titanium diphenyl or dichloride,  
14 bis(methylcyclopentadienyl)titanium diphenyl or dihalides; dialkyl,  
15 trialkyl, tetra-alkyl and penta-alkyl cyclopentadienyl titanium  
16 compounds such as bis(1,2-dimethylcyclopentadienyl)titanium diphenyl  
17 or dichloride, bis(1,2-diethylcyclopentadienyl)titanium diphenyl or  
18 dichloride and other dihalide complexes; silicon, phosphine, amine or  
19 carbon bridged cyclopentadiene complexes, such as dimethyl  
20 silyldicyclopentadienyl titanium diphenyl or dichloride, methyl  
21 phosphine dicyclopentadienyl titanium diphenyl or dichloride,  
22 methylenedicyclopentadienyl titanium diphenyl or dichloride and other  
23 dihalide complexes and the like.

24 Additional zirconocene catalysts useful according to the  
25 present invention include bis(cyclopentadienyl) zirconium dimethyl;  
26 bis(cyclopentadienyl) zirconium dichloride, bis(cyclopentadienyl)  
27 zirconium methylchloride. Illustrative but non-limiting examples of  
28 the zirconocenes Formula II and III which can be usefully employed in  
29 accordance with this invention are, pentamethylcyclopentadienyl  
30 zirconium trichloride, pentaethylcyclopentadienyl zirconium  
31 trichloride, bis(pentamethylcyclopentadienyl)zirconium diphenyl, the  
32 alkyl substituted cyclopentadienes, such as bis(ethyl  
33 cyclopentadienyl)zirconium dimethyl,  
34 bis( $\beta$ -phenylpropylcyclopentadienyl)zirconium dimethyl,  
35 bis(methylcyclopentadienyl)zirconium dimethyl,  
36 bis(n-butyl-cyclopentadienyl)zirconium dimethyl,  
37 bis(cyclohexylmethylcyclopentadienyl)zirconium dimethyl.

1 bis(n-octyl-cyclopentadienyl)zirconium dimethyl, and haloalkyl and  
2 dihalide complexes of the above; di-alkyl, trialkyl, tetra-alkyl, and  
3 penta-alkyl cyclopentadienes, such as bis(pentamethylcyclopentadienyl)  
4 zirconium di-methyl, bis(1,2-dimethylcyclopentadienyl)zirconium  
5 dimethyl and dihalide complexes of the above; silicone, phosphorus,  
6 and carbon bridged cyclopentadiene complexes such as  
7 dimethylsilyldicyclopentadienyl zirconium dimethyl or dihalide, and  
8 methylene dicyclopentadienyl zirconium dimethyl or dihalide, and  
9 methylene dicyclopentadienyl zirconium dimethyl or dihalide, carbenes  
10 represented by the formula  $\text{Cp}_2\text{Zr}=\text{CHP}(\text{C}_6\text{H}_5)_2\text{CH}_3$ , and  
11 derivatives of these compounds such as  $\text{Cp}_2\text{ZrCH}_2\text{CH}(\text{CH}_3)\text{CH}_2$ .

12 Bis(cyclopentadienyl)hafnium dichloride,  
13 bis(cyclopentadienyl)hafnium dimethyl, bis(cyclopentadienyl)vanadium  
14 dichloride and the like are illustrative of other metallocenes.

15 The inorganic oxide support used in the preparation of the  
16 catalyst may be any particulate oxide or mixed oxide as previously  
17 described which has been thermally or chemically dehydrated such that  
18 it is substantially free of adsorbed moisture.

19 The specific particle size, surface area, pore volume, and  
20 number of surface hydroxyl groups characteristic of the inorganic  
21 oxide are not critical to its utility in the practice of the  
22 invention. However, since such characteristics determine the amount  
23 of inorganic oxide that it is desirable to employ in preparing the  
24 catalyst compositions, as well as affecting the properties of polymers  
25 formed with the aid of the catalyst compositions, these  
26 characteristics must frequently be taken into consideration in  
27 choosing an inorganic oxide for use in a particular aspect of the  
28 invention. For example, when the catalyst composition is to be used  
29 in a gas-phase polymerization process - a type of process in which it  
30 is known that the polymer particle size can be varied by varying the  
31 particle size of the support - the inorganic oxide used in preparing  
32 the catalyst composition should be one having a particle size that is  
33 suitable for the production of a polymer having the desired particle  
34 size. In general, optimum results are usually obtained by the use of  
35 inorganic oxides having an average particle size in the range of about  
36 30 to 600 microns, preferably about 30 to 100 microns; a surface area  
37 of about 50 to 1,000 square meters per gram, preferably about 100 to

1 400 square meters per gram; and a pore volume of about 0.5 to 3.5 cc  
2 per gram; preferably about 0.5 to 2cc per gram.

3 The polymerization may be conducted by a solution, slurry, or  
4 gas-phase technique, generally at a temperature in the range of about  
5 0°-160°C or even higher, and under atmospheric, subatmospheric, or  
6 superatmospheric pressure conditions; and conventional polymerization  
7 adjuvants, such as hydrogen may be employed if desired. It is  
8 generally preferred to use the catalyst compositions at a  
9 concentration such as to provide about 0.000001 - 0.005%, most  
10 preferably about 0.00001 - 0.0003%, by weight of transition metal  
11 based on the weight of monomer(s), in the polymerization of ethylene,  
12 alone or with one or more higher olefins.

13 A slurry polymerization process can utilize sub- or super-  
14 atmospheric pressures and temperatures in the range of 40-110°C. In a  
15 slurry polymerization, a suspension of solid, particulate polymer is  
16 formed in a liquid polymerization medium to which ethylene,  
17 alpha-olefin comonomer, hydrogen and catalyst are added. The liquid  
18 employed as the polymerization medium can be an alkane or cycloalkane,  
19 such as butane, pentane, hexane, or cyclohexane, or an aromatic  
20 hydrocarbon, such as toluene, ethylbenzene or xylene. The medium  
21 employed should be liquid under the conditions of the polymerization  
22 and relatively inert. Preferably, hexane or toluene is employed.

23 A gas-phase polymerization process utilizes superatmospheric  
24 pressure and temperatures in the range of about 50°-120°C. Gas-phase  
25 polymerization can be performed in a stirred or fluidized bed of  
26 catalyst and product particles in a pressure vessel adapted to permit  
27 the separation of product particles from unreacted gases.  
28 Thermostated ethylene, comonomer, hydrogen and an inert diluent gas  
29 such as nitrogen can be introduced or recirculated so as to maintain  
30 the particles at a temperature of 50°-120°C. Triethylaluminum may be  
31 added as needed as a scavenger of water, oxygen, and other  
32 adventitious impurities. Polymer product can be withdrawn  
33 continuously or semi-continuing at a rate such as to maintain a  
34 constant product inventory in the reactor. After polymerization and  
35 deactivation of the catalyst, the product polymer can be recovered by  
36 any suitable means. In commercial practice, the polymer product can  
37 be recovered directly from the gas phase reactor, freed of residual

1 monomer with a nitrogen purge, and used without further deactivation  
2 or catalyst removal. The polymer obtained can be extruded into water  
3 and cut into pellets or other suitable comminuted shapes. Pigments,  
4 antioxidants and other additives, as is known in the art, may be added  
5 to the polymer.

6 The molecular weight of polymer product obtained in  
7 accordance with this invention can vary over a wide range, such as low  
8 as 500 up to 2,000,000 or higher and preferably 1,000 to about  
9 500,000.

10 For the production of polymer product having a narrow  
11 molecular weight distribution, it is preferable to deposit only one  
12 metallocene on to the inert porous support material and employ said  
13 support metallocene together with the alumoxane as the polymerization  
14 catalyst.

15 It is highly desirable to have for many applications, such as  
16 extrusion and molding processes, polyethylenes which have a broad  
17 molecular weight distribution of the unimodal and/or the multimodal  
18 type. Such polyethylenes evidence excellent processability, i.e. they  
19 can be processed at a faster throughput rate with lower energy  
20 requirements and at the same time such polymers would evidence reduced  
21 melt flow perturbations. Such polyethylenes can be obtained by  
22 providing a catalyst component comprising at least two different  
23 metallocenes, each having different propagation and termination rate  
24 constants for ethylene polymerizations. Such rate constants are  
25 readily determined by one of ordinary skill in the art.

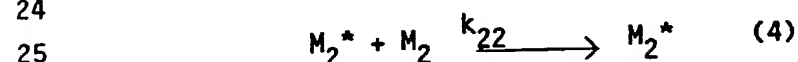
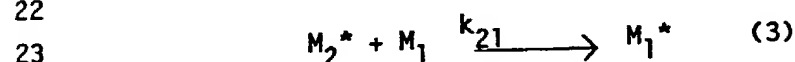
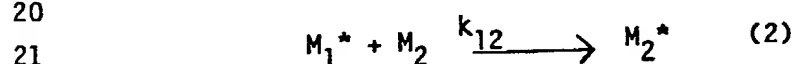
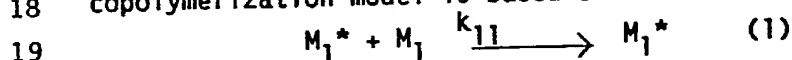
26 The molar ratio of the metallocenes, such as, for example, of  
27 a zirconocene to a titanocene in such catalysts, can vary over a wide  
28 range, and in accordance with this invention, the only limitation on  
29 the molar ratios is the breadth of the Mw distribution or the degree  
30 of bimodality desired in the product polymer. Desirably, the  
31 metallocene to metallocene molar ratio will be about 1:100 to about  
32 100:1, and preferably 1:10 to about 10:1.

33 The present invention also provides a process for producing  
34 (co)polyolefin reactor blends comprising polyethylene and  
35 copolyethylene- $\alpha$ -olefins. The reactor blends are obtained  
36 directly during a single polymerization process, i.e., the blends of  
37 this invention are obtained in a single reactor by simultaneously

1 polymerizing ethylene and copolymerizing ethylene with an alpha-olefin  
 2 thereby eliminating expensive blending operations. The process of  
 3 producing reactor blends in accordance with this invention can be  
 4 employed in conjunction with other prior art blending techniques, for  
 5 example, the reactor blends produced in a first reactor can be  
 6 subjected to further blending in a second stage by use of the series  
 7 reactors.

8 In order to produce reactor blends the supported metallocene  
 9 catalyst component comprises at least two different metallocenes each  
 10 having different comonomer reactivity ratios.

11 The comonomer reactivity ratios of the metallocenes in  
 12 general are obtained by well known methods, such as for example, as  
 13 described in "Linear Method for Determining Monomer Reactivity Ratios  
 14 in Copolymerization", M. Fineman and S. D. Ross, J. Polymer Science 5,  
 15 259 (1950) or "Copolymerization", F. R. Mayo and C. Walling, Chem.  
 16 Rev. 46, 191 (1950) incorporated herein in its entirety by reference.  
 17 For example, to determine reactivity ratios the most widely used  
 18 copolymerization model is based on the following equations:



23 where  $M_i$  refers to a monomer molecule which is arbitrarily  
 24 designated  $i$  (where  $i = 1, 2$ ) and  $M_i^*$  refers to a growing polymer  
 25 chain to which monomer  $i$  has most recently attached.

26 The  $k_{ij}$  values are the rate constants for the indicated  
 27 reactions. In this case,  $k_{11}$  represents the rate at which an  
 28 ethylene unit inserts into a growing polymer chain in which the  
 29 previously inserted monomer unit was also ethylene. The reactivity  
 30 rates follow as:  $r_1 = k_{11}/k_{12}$  and  $r_2 = k_{22}/k_{21}$   
 31 wherein  $k_{11}$ ,  $k_{12}$ ,  $k_{22}$  and  $k_{21}$  are the rate constants for  
 32 ethylene (1) or comonomer (2) addition to a catalyst site where the  
 33 last polymerized monomer is ethylene ( $k_{1X}$ ) or comonomer (2) ( $k_{2X}$ ).  
 34 Since, in accordance with this invention, one can produce

35  
 36  
 37

1 high viscosity polymer product at a relatively high temperature,  
2 temperature does not constitute a limiting parameter as with the prior  
3 art metallocene/alumoxane catalyst. The catalyst systems described  
4 herein, therefore, are suitable for the polymerization of olefins in  
5 solution, slurry or gas phase polymerizations and over a wide range of  
6 temperatures and pressures. For example, such temperatures may be in  
7 the range of about -60°C to about 280°C and especially in the range of  
8 about 0°C to about 160°C. The pressures employed in the process of  
9 the present invention are those well known, for example, in the range  
10 of about 1 to 500 atmospheres, however, higher pressures can be  
11 employed.

12 The polymers produced by the process of this present  
13 invention are capable of being fabricated into a wide variety of  
14 articles, as is known for homopolymers of ethylene and copolymers of  
15 ethylene and higher alpha-olefins.

16 In a slurry phase polymerization, the alkyl aluminum  
17 scavenger is preferably dissolved in a suitable solvent, typically in  
18 an inert hydrocarbon solvent such as toluene, xylene, and the like in  
19 a molar concentration of about  $5 \times 10^{-3}$  M. However, greater or lesser  
20 amounts can be used.

21 Bis(cyclopentadienyl)hafnium dichloride,  
22 bis(cyclopentadienyl)hafnium dimethyl, bis(cyclopentadienyl)vanadium  
23 dichloride and the like are illustrative of other metallocenes.

24 Various inorganic oxide supports may be used for supported  
25 catalyst systems to prepare polymers of the present invention. The  
26 polymerizations are generally carried in the temperature range of  
27 about 0-160°C or even higher but this range is not meant to be  
28 exclusive for preparing the polymers of the invention which may be  
29 prepared by any technique resulting in the structure set forth.  
30 Atmospheric, sub-atmospheric, or super-atmospheric pressure conditions  
31 may exist for the polymerization using the metallocene catalyst  
32 described above. It is generally preferred to use catalyst  
33 compositions at a concentration so as to provide from about 1 ppm to  
34 about 5000 ppm, most preferably 10 ppm to 300 ppm, by weight of  
35 transition metal based on the weight of monomers in the polymerization  
36 of the ethylene polymers.

1           A slurry polymerization process may generally use  
2 sub-atmospheric or super-atmospheric pressures and temperatures in the  
3 range of 40-110°C. In a slurry polymerization, a suspension of solid,  
4 particulate polymer is formed in a liquid polymerization medium to  
5 which ethylene and comonomers and often hydrogen along with catalyst  
6 are added. The liquid employed in the polymerization medium can be  
7 alkane or cycloalkane, or an aromatic hydrocarbon such as toluene,  
8 ethylbenzene or xylene. The medium employed should be liquid under  
9 the conditions of polymerization and relatively inert. Preferably,  
10 hexane or toluene is employed.

11           In a modification, polymers of the present invention may be  
12 formed by gas-phase polymerization. A gas-phase process utilizes  
13 super-atmospheric pressure and temperatures in the range of about  
14 50°-120°C. Gas-phase polymerization can be performed in a stirred or  
15 fluidized bed of catalyst and product particles in a pressure vessel  
16 adapted to permit the separation of product particles from unreacted  
17 gases. Thermostated ethylene, comonomer (including diene), hydrogen  
18 and an inert diluent gas such as nitrogen can be introduced or  
19 recirculated so as to maintain the particles at a temperature of  
20 50°-120°C. Triethylaluminum may be added as needed as a scavenger of  
21 water, oxygen, and other adventitious impurities. Polymer product can  
22 be withdrawn continuously or semi-continuing at a rate such as to  
23 maintain a constant product inventory in the reactor. After  
24 polymerization and deactivation of the catalyst, the product polymer  
25 can be recovered by any suitable means. In commercial practice, the  
26 polymer product can be recovered directly from the gas phase reactor,  
27 freed of residual monomer with a nitrogen purge, and used without  
28 further deactivation or catalyst removal. The polymer obtained can be  
29 extruded into water and cut into pellets or other suitable comminuted  
30 shapes. Pigments, antioxidants and other additives, as is known in  
31 the art, may be added to the polymer.

32           The molecular weight of polymer product obtained in  
33 accordance with this invention can vary over a wide range, as low as  
34 500 up to 2,000,000 or higher and preferably 1,000 to about 500,000.

35           For the production of polymer product having a narrow  
36 molecular weight distribution, it is preferable to deposit only one  
37 metallocene on to the inert porous support material and employ said

1 support metallocene together with the alumoxane as the polymerization  
2 catalyst.

3 It is highly desirable to have for many applications, such  
4 as extrusion and molding processes, polyethylenes which have a broad  
5 molecular weight distribution of the unimodal and/or the multimodal  
6 type. Such polyethylenes evidence excellent processability, i.e.  
7 they can be processed at a faster throughput rate with lower energy  
8 requirements and at the same time such polymers would evidence  
9 reduced melt flow perturbations. Such polyethylenes can be obtained  
10 by providing a catalyst component comprising at least two different  
11 metallocenes, each having different propagation and termination rate  
12 constants for ethylene polymerizations. Such rate constants are  
13 readily determined by one of ordinary skill in the art.

14 The molar ratio of the metallocenes, such as, for example,  
15 of a zirconocene to a titanocene in such catalysts, can vary over a  
16 wide range, and in accordance with this invention, the only  
17 limitation on the molar ratios is the breadth of the Mw distribution  
18 or the degree of bimodality desired in the product polymer.  
19 Desirably, the metallocene to metallocene molar ratio will be about  
20 1:100 to about 100:1, and preferably 1:10 to about 10:1.

21 The present invention is illustrated by the following  
22 examples.

### 23 Examples

24 In the Examples following the alumoxane employed was  
25 prepared by adding 76.5 grams ferrous sulfate heptahydrate in 4  
26 equally spaced increments over a 2 hour period to a rapidly stirred 2  
27 liter round-bottom flask containing 1 liter of a 13.1 weight percent  
28 solution of trimethylaluminum (TMA) in toluene. The flask was  
29 maintained at 50°C and under a nitrogen atmosphere. Methane produced  
30 was continuously vented. Upon completion of the addition of ferrous  
31 sulfate heptahydrate the flask was continuously stirred and  
32 maintained at a temperature of 50°C for 6 hours. The reaction  
33 mixture was cooled to room temperature and was allowed to settle.  
34 The clear solution containing the alumoxane was separated by  
35 decantation from the insoluble solids.

36 Molecular weights were determined on a Water's Associates  
37 Model No. 150C GPC (Gel Permeation Chromatography). The measurements

1 were obtained by dissolving polymer samples in hot trichlorobenzene  
2 and filtered. The GPC runs are performed at 145°C in  
3 trichlorobenzene at 1.0 ml/min flow using styragel columns from  
4 Perkin Elmer, Inc. 0.1% solutions (300 microliters of  
5 trichlorobenzene solution) were injected and the samples were run in  
6 duplicate. The integration parameters were obtained with a  
7 Hewlett-Packard Data Module.

#### 8 Catalyst Preparation

##### 9 Catalyst A

10 10 grams of a high surface area (Davison 952) silica,  
11 dehydrated in a flow of dry nitrogen at 800°C for 5 hours, was  
12 slurried with 50 cc of toluene at 25°C under nitrogen in a 250 cc  
13 round-bottom flask using a magnetic stirrer. 25 cc of methyl  
14 alumoxane in toluene (1.03 moles/liter in aluminum) was added  
15 dropwise over 5 minutes with constant stirring to the silica slurry.  
16 Stirring was continued for 30 minutes while maintaining the  
17 temperature at 25°C at which time the toluene was decanted off and  
18 the solids recovered. To the alumoxane treated silica was added  
19 dropwise over 5 minutes, with constant stirring 25.0 cc of a toluene  
20 solution containing 0.200 gram of dicyclopentadienyl zirconium  
21 dichloride. The slurry was stirred an additional 1/2 hour while  
22 maintaining the temperature at 25°C and thereafter the toluene was  
23 decanted and the solids recovered and dried in vacuo for 4 hours.  
24 The recovered solid was neither soluble nor extractable in hexane.  
25 Analysis of the catalyst indicated that it contained 4.5 weight  
26 percent aluminum and 0.63 weight percent zirconium.

##### 27 Catalyst B

28 This catalyst will demonstrate that the use of the catalyst  
29 of this invention in the production of copolyethylene with 1-butene  
30 results in the more efficient incorporation of 1-butene as  
31 demonstrated by the polymer product density.

32 The procedure for the preparation of Catalyst A was followed  
33 with the exception that the methylalumoxane treatment of the support  
34 material was eliminated. Analysis of the recovered solid indicated  
35 that it contained 0.63 weight percent zirconium and 0 weight percent  
36 aluminum.

1     Catalyst C

2             The procedure for the preparation of Catalyst A was followed  
3     except that 0.300 of bis(cyclopentadienyl) zirconium dimethyl was  
4     substituted for the bis(cyclopentadienyl) zirconium dichloride.  
5     Analysis of the recovered solid indicated that it contained 4.2  
6     weight percent aluminum and 1.1 weight percent zirconium.

7     Catalyst D

8             The procedure for preparation of Catalyst A was followed  
9     with the exception that 0.270 g of bis(n-butyl-cyclopentadienyl)  
10    zirconium  
11    dichloride was substituted for the bis(cyclopentadienyl) zirconium  
12    dichloride of Catalyst A and all procedures were performed at 80°C.  
13    Analysis of the recovered solids indicated that it contained 0.61  
14    weight percent zirconium and 4.3 weight percent aluminum.

15    Catalyst E

16            The procedure for preparation of Catalyst D was followed with  
17    the exception that 0.250 grams of  
18    bis(n-butyl-cyclopentadienyl)zirconium dimethyl was substituted for  
19    the metallocene dichloride. Analysis of the recovered solid indicated  
20    that it contained 0.63 weight percent zirconium and 4.2 weight percent  
21    aluminum.

22    Catalyst F

23            The procedure for the preparation of Catalyst D was followed  
24    with the exception that .500 grams of  
25    bis(pentamethylcyclopentadienyl)zirconium dichloride was substituted  
26    for the metallocene. Analysis of the recovered solid indicated that  
27    it contained 0.65 weight percent zirconium and 4.7 weight percent  
28    aluminum.

29    Catalyst X

30            10 gms of a high surface area (Davison 952) silica,  
31    dehydrated in a flow of dry nitrogen at 800°C for 5 hours, was  
32    slurried with 50 cc of toluene at 25°C under nitrogen in a 250 cc  
33    round-bottom flask using a magnetic stirrer. 25 cc of methyl  
34    alumoxane in toluene (1.03 moles/liter in aluminum) was added dropwise  
35    over 5 minutes with constant stirring to the silica slurry. Stirring  
36    was continued for 30 minutes while maintaining the temperature at 60°C  
37    at which time the toluene was decanted off and the solids recovered.

1 To the alumoxane, treated silica was added dropwise over 5 minutes,  
2 with constant stirring 25.0 cc of a toluene solution containing 0.200  
3 grams of bis(n-butyl-cyclopentadienyl) zirconium dichloride. The  
4 slurry was stirred an additional 1/2 hour while maintaining the  
5 temperature at 60°C and thereafter the toluene was decanted and the  
6 solids recovered and dried in vacuo for 4 hours. The recovered solid  
7 was neither soluble nor extractable in hexane. Analysis of the  
8 catalyst indicated that it contained 4.5 weight percent aluminum and  
9 0.63 weight percent zirconium.

10 The following examples show preparation of copolymers of the  
11 invention from ethylene and butadiene. Catalyst systems, especially  
12 of the metallocene/alumoxane type are effective for preparation of the  
13 polymers. A better understanding of the invention will be had by a  
14 review of the examples in conjunction with the drawing figures. The  
15 best mode of the invention now known to us is disclosed herein.

16 Example 1 (Diluent Polymerization):

17 A 2-liter stainless steel pressure vessel, equipped with an  
18 incline blade stirrer, an external water jacket for temperature  
19 control, a septum inlet and vent line, and a regulated supply of dry  
20 ethylene and nitrogen, was dried and deoxygenated with a nitrogen  
21 flow. 800cc of dry, degassed isopentane and 200cc of purified  
22 1,3-butadiene was injected directly into the pressure vessel. 15.0cc  
23 of 0.785 molar (in total aluminum) methyl alumoxane in toluene was  
24 injected into the vessel by a gas tight syringe through the septum  
25 inlet and the mixture was stirred at 1,200 rpm's and 82°C for 5  
26 minutes at 0 psig of nitrogen. Bis(n-butylcyclopentadienyl) zirconium  
27 dichloride (300 mg) dissolved in 3.00 ml of dry, distilled toluene was  
28 injected through the septum inlet into the vessel. After 1 minute,  
29 ethylene at 120 psig was admitted while the reaction vessel was  
30 maintained at 82°C. The ethylene was passed into the vessel for 20  
31 minutes at which time the reaction was stopped by rapidly venting and  
32 cooling. 33.1 gms of ethylene/butadiene copolymer was recovered after  
33 evaporation of the liquid components under nitrogen. The polymer was  
34 analyzed by C<sup>13</sup>NMR and it was found that for each cis 1,4 unit (cis  
35 vinylene in the chain) in the polymer, there were 0.6 of 1,2 units  
36 (pendant vinyl group on the chain); 4.7 of trans-1,4 units (trans  
37 vinylene in the chain) and 8.7 of cyclopentane rings (connected in the

1 ethylene chain at 1,2 on the ring).

2 Example 1A (Diluent Polymerization):

3 A 1-liter stainless pressure vessel, equipped with an incline  
4 blade stirrer, an external water jacket for temperature control, a  
5 septum inlet and vent line, and a regulated supply of dry ethylene and  
6 nitrogen, was dried and deoxygenated with a nitrogen flow. 500cc of  
7 dry, degassed toluene and 80cc of purified 1-hexene, and 200 cc of  
8 purified 1,3-butadiene were injected directly into the pressure  
9 vessel. 10.0cc of 0.785 molar (in total aluminum) methyl alumoxane in  
10 toluene was injected into the vessel by a gas tight syringe through  
11 the septum inlet and the mixture was stirred at 1,200 rpm's and 70°C  
12 for 5 minutes at 0 psig of nitrogen. Bis(n-butylcyclopentadienyl)  
13 zirconium dichloride (0.10 mg) dissolved in 0.10 ml of dry, distilled  
14 toluene was injected through the septum inlet into the vessel. After  
15 1 minute, ethylene at 75 psig was admitted while the reaction vessel  
16 was maintained at 70°C. The ethylene was passed into the vessel for  
17 20 minutes at which time the reaction was stopped by rapidly venting  
18 and cooling. 15.5 gms of ethylene-1-hexene-1,3-butadiene terpolymer  
19 was recovered after evaporation of the liquid components under  
20 nitrogen.

21 Example 2 (Gas Phase Polymerization):

22 Polymerization was performed in the gas phase in a 1-liter  
23 autoclave reactor equipped with a paddle stirrer, an external water  
24 jacket for temperature control, a septum inlet and a regulated supply  
25 of dry nitrogen, ethylene, hydrogen and 1-butene. The reactor,  
26 containing 40.0 g of granular polypropylene (> 600 micron particle  
27 size) which was added to aid stirring in the gas phase, was dried and  
28 degassed thoroughly at 85°C. As a scavenger, 0.3 cc of a 20 weight  
29 percent triethylaluminum solution in hexane was injected through the  
30 septum inlet, into the vessel using a gas-tight syringe in order to  
31 remove traces of oxygen and water. The reactor contents were stirred  
32 at 120 rpm at 85°C for 1 minute at 0 psig nitrogen pressure. 9.4  
33 grams of 1,3-butadiene liquid was injected. 500.0 mg of Catalyst X  
34 was injected into the reactor and the reactor was pressured to 200  
35 psig with ethylene. The polymerization was continued for 20 minutes  
36 while maintaining the reaction vessel at 85°C and 200 psig by constant  
37 ethylene flow. The reaction was stopped by rapidly cooling and

1 venting. 5.6 grams of ethylene-1,3-butadiene copolymer was  
2 recovered. The polyethylene was recovered by sieving out the fraction  
3 which had a particle size greater than 350 micron diameter. The  
4 polymer was analyzed by  $C^{13}$  NMR and it was found that for each  
5 cis-1,4 unit incorporated, there were no 1,2 units; 8 trans-1,4 units;  
6 and 14.9 cyclopentane rings (connected in the ethylene chain at 1,2 on  
7 the ring).

#### 8 Example 3 - Polymerization - Catalyst A

9 Polymerization performed in the gas phase in a 1-liter  
10 autoclave reactor equipped with a paddle stirrer, an external water  
11 jacket for temperature control, a septum inlet and a regulated supply  
12 of dry nitrogen, ethylene, hydrogen and 1-butene. The reactor,  
13 containing 40.0 g of ground polystyrene (10 mesh) which was added to  
14 aid stirring in the gas phase, was dried and degassed thoroughly at  
15 85°C. As a scavenger, 2.00 cc of a methyl alumoxane solution (0.64  
16 molar in total aluminum) was injected through the septum inlet, into  
17 the vessel using a gas-tight syringe in order to remove traces of  
18 oxygen and water. The reactor contents were stirred at 120 rpm at  
19 85°C for 1 minute at 0 psig nitrogen pressure. 500.0 mg of Catalyst A  
20 was injected into the reactor and the reactor was pressured to 200  
21 psig with ethylene. The polymerization was continued for 10 minutes  
22 while maintaining the reaction vessel at 85°C and 200 psig by constant  
23 ethylene flow. The reaction was stopped by rapidly cooling and  
24 venting. 12.3 grams of polyethylene were recovered. The polyethylene  
25 was recovered by stirring the product with 1 liter of dichloromethane  
26 at 40°C, filtering and washing with dichloromethane to recover the  
27 insoluble polyethylene product from the soluble polystyrene stirring  
28 aid. The polyethylene had a molecular weight of 146,000.

#### 29 Example 4 - Polymerization - Catalyst A

30 Polymerization was performed as in Example 3 in the presence  
31 of Catalyst A except that 3.0 psig of hydrogen was pressured into the  
32 reactor prior to ethylene injection. 13.2 grams of polyethylene were  
33 recovered having a molecular weight of 29,000.

#### 34 Example 5 - Polymerization - Catalyst A

35 Polymerization was performed as in Example 3 in the presence  
36 of Catalyst A except that 13.0 cc (0.137 moles) of 1-butene was  
37 pressured into the reactor together with the ethylene after the

1 catalyst injection. 13.8 grams of polyethylene were recovered having  
2 a molecular weight of 39,000 and a density of 0.918 g/cc.

3 Comparative Example 5A - Polymerization - Catalyst B

4 The polymerization was performed as in Example 3 with the  
5 exception that Catalyst B was substituted for Catalyst A. 17.3 g of  
6 polyethylene were recovered having a molecular weight of 67,000 and a  
7 density of 0.935 g/cc. The higher density as compared with that  
8 obtained in Example 3 demonstrates the less efficient incorporation of  
9 comonomer.

10 Example 6 - Polymerization - Catalyst C

11 Polymerization was performed as in Example 3 with the  
12 exception that Catalyst C was used in place of Catalyst A. 9.8 grams  
13 of polyethylene were recovered having a molecular weight of 189,000  
14 and a density of 0.960 g/cc.

15 Example 7 - Polymerization - Catalyst C

16 Polymerization was performed as in Example 6 except that 13.0  
17 cc of 1-butene (0.123 moles) and 0.6 psig of hydrogen (1.66  
18 millimoles) was introduced after the catalyst together with the  
19 ethylene. 6.5 grams of polyethylene were recovered having a molecular  
20 weight of 41,000 and a density of 0.926 g/cc.

21 Example 8 - Polymerization - Catalyst C

22 Polymerization was performed as in Example 6, except that the  
23 scavenger methyl alumoxane was eliminated and no other aluminumalkyl  
24 scavenger was injected. 10.2 grams of polyethene was recovered having  
25 a molecular weight of 120,000 and a density of 0.960 g/cc.

26 Example 9 - Polymerization - Catalyst D

27 Polymerization was performed as in Example 3 with the  
28 exception that 0.6 cc of a 25 weight percent triethylaluminum in  
29 hexane was substituted for the methylalumoxane solution of Example 1,  
30 and Catalyst D was employed in place of Catalyst A. 50.4 g of  
31 polyethylene was recovered having a molecular weight of 196,000 and a  
32 density of 0.958 g/cc.

33 Example 10 - Polymerization - Catalyst D

34 Polymerization was performed as in Example 3 with the  
35 exception that the scavenger, methylalumoxane was eliminated, Catalyst  
36 D was employed in place of Catalyst A and the polymerization was  
37 stopped at the end of 5 minutes. 28.8 g of polyethylene was recovered

1 having a molecular weight of 196,000 and a density of 0.958 g/cc.

2 Example 11 - Polymerization - Catalyst E

3 Polymerization was performed as in Example 10 using Catalyst  
4 E with no scavenger aluminum compound. 24.0 grams of polyethylene was  
5 recovered having a weight average molecular weight of 190,000, a  
6 number average molecular weight of 76,000 and a density of 0.958  
7 g/cc.

8 Example 12 - Polymerization - Catalyst F

9 Polymerization was performed as in Example 9 except that .500  
10 grams of Catalyst F was substituted for Catalyst D. 8.1 grams of  
11 polyethylene was recovered having a molecular weight of 137,000 and a  
12 density of 0.960 g/cc.

13 The storage ( $G'$ ) and loss ( $G''$ ) moduli of the polymers of  
14 Examples 1 was measured at 150°C and 200°C on a Rheometrics  
15 System-Four mechanical spectrometer to determine the presence of long  
16 chain branching in the polymer composition as produced in the  
17 reactor. A one-gram (approximately) sample was washed in a dissolve  
18 and precipitate process to deash and then stabilized with 1000 ppm BHT.

19 Three criteria are used to decide whether a polyethylene  
20 resin contains long chain branching:

21 (i) Melt elasticity, which is high for long chain branched  
22 polymers and low for linear molecule polymers, was evaluated from  
23 storage moduli in the low frequency region.

24 (ii) Activation energy, which is about 14 Kcal/mole for long  
25 chain branched polymers and about 6 Kcal/mole for linear molecule  
26 polymers was calculated from the shifting factor of the  $G'$  and  $G''$   
27 spectra at two different temperatures.

28 (iii) Thermorheological characteristics, which are complex for  
29 long chain branched polymers and simple for linear molecule polymers,  
30 were assessed by comparing the shifting factors at different  
31 frequencies (rotation).

32 The results given below indicate that the copolymer of  
33 Example 1 has significant long chain branching.

Rheological Data

	<u>Rheological Data</u>		
	<u>Melt Elasticity</u>	<u>Viscous Activation Energy (Kcal/mole)</u>	<u>Thermo-Rheological Characterization</u>
Example 1	High	More than 10	Complex

The structural characterization of the polymers of the invention and the comparative product are set forth in the Table below. A review of the information and the Table discloses that the polymers of the invention have improved structural properties based upon their molecular weight distribution, and/or comonomer distribution, and/or cluster index. Furthermore, the copolymers of the invention are not gels but are boiling xylene-soluble polymers.

The polymer from Example 1 is indicated to have long chain branches including intermolecular coupling but is not crosslinked gel.

The polymers of the invention were tested for degree of unsaturation by an infrared procedure wherein concentrations of unsaturation in the ethylene-based polymers was determined by comparison of IR spectra of brominated versus original polymer specimens utilizing the following bands:

Vinylene - 965 centimeters<sup>-1</sup>  
Vinyl - 909 centimeters<sup>-1</sup>  
Vinylidene - 888 centimeters<sup>-1</sup>

The procedure for determination of unsaturation is known to the skilled artisan.

Thus, the present invention constitutes a method and copolymer wherein the copolymer has either no long chain branching and intermolecular coupling or a controlled degree of intermolecular coupling without forming a crosslinked product. The copolymers of the invention have significant utility in the various applications to which ethylene polymers and copolymers are customarily assigned.

TABLE

RESIN	COMONOMER CONTENT (MOLE PERCENT)				$M_w$ ( $\times 10^3$ )	$M_w/M_n$	COMPOSITION DISTRIBUTION	CLUSTER INDEX	MELTING BEHAVIOUR	
	TYPE	AMOUNT	TYPE	AMOUNT					DISTRIBUTION	PEAK M.P. ( $^{\circ}$ C)
EXAMPLE 1	BUTADIENE	1.5	-	-	107.4	2.50	NARROW	5.0	NARROW	114.3
EXAMPLE 1A	BUTADIENE	1.2	HEXENE-1	1.9	161.5	2.00	-	5.0	NARROW	104.4
EXAMPLE 2	BUTADIENE	1.3	-	-	152.6	4.70	-	5.0	NARROW	115.0
3 - EXXON LL 3001	HEXENE-1	3.7	-	-	103.1	3.30	BROAD	12.1	BROAD	124.6
4 - DOWLEX 2045	OCTENE-1	2.8	-	-	114.6	3.67	BROAD	9.5	BROAD	124.3
5 - EXXON LL 1001	BUTENE-1	4.4	-	-	118.0	3.33	BROAD	11.7	BROAD	121.6
6 - DUPONT SCLAIR 110	BUTENE-1	3.3	-	-	115.7	3.79	BROAD	5.0	BROAD	118.7
7 - MITSUI 2020L	4-METHYL- PENTENE-1	3.5	-	-	92.3	2.6	BROAD	-	BROAD	124.5
8 - LLDPE <sup>1</sup>	BUTENE-1	5.2	-	-	96.1	1.78	NARROW	9.6	NARROW	94.0

1. LABORATORY PREPARATION WITH A SOLUBLE VANADIUM OXYCHLORIDE/ETHYL ALUMINUM SESQUICHLORIDE CATALYST.

CLAIMS:

1. A copolymer from the polymerization of ethylene and at least one other polymerizable comonomer comprising 1,3-butadiene, said copolymer incorporating in its structure at least about 3 mole percent of said at least one polymerizable comonomer and having a cluster index of about 9 or less.

2. The copolymer of claim 1 incorporating in its structure at least about 5 mole percent of said polymerizable copolymer.

3. The copolymer of claim 1 wherein said at least one polymerizable copolymer also comprises an alpha olefin.

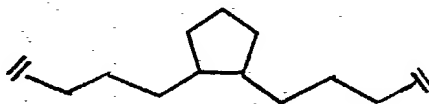
4. The copolymer of claim 3 wherein said butadiene is incorporated in at least about 0.1 mole percent.

5. The copolymer of claim 1 wherein said at least one polymerizable comonomer consists essentially of said butadiene.

6. A copolymer of claim 1 having a molecular weight distribution ( $M_w/M_n$ ) of about 3.0 or less.

7. The composition of claim 1 wherein the majority of said butadiene is incorporated in the polyethylene chain as cyclopentane structure I:

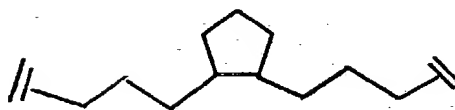
(I)



8. The composition of claim 1 having a molecular weight ( $M_n$ ) of about 500 to about 1,000,000.
9. The composition of claim 1 incorporating at least about 5 mole percent of said butadiene.
10. The composition of claim 1 having a cluster index of about 5 or less.
11. The composition of claim 8 having a molecular weight ( $M_n$ ) of about 500-200,000 and being substantially entirely devoid of long chain branching.
12. The composition of claim 1 having a composition distribution wherein at least about 55 weight percent of the copolymer composition molecules have a comonomer content within about 50% of the median comonomer content in mole percent of said copolymer composition.
13. The composition of claim 12 wherein at least about 70 weight percent of the copolymer molecules have a comonomer content within about 50% of the median comonomer content in mole percent of said composition.
14. A copolymer comprising ethylene and at least about 3 mole percent butadiene having a molecular weight of about 500-1,000,000, a molecular weight distribution ( $M_w/M_n$ ) of about 3.0 or less, a composition distribution wherein at least about 55 weight percent of the copolymer molecules have a comonomer content within 50% of the median comonomer content in mole percent, of said copolymer composition, and a cluster index of 9 or less, said

copolymer having most of said butadiene incorporated as cyclopentane structure I:

(I)



15. A method for preparing copolymers of ethylene and butadiene comprising carrying out the polymerization in the presence of a metallocene/alumoxane catalyst system and forming an uncross-linked ethylene/butadiene copolymer composition.

16. The method of claim 15 comprising copolymerizing 50-99 mole parts ethylene, 1-50 mole parts butadiene, and 0-50 mole parts polymerizable termonomer.

17. The method of claim 16 wherein said polymerizable termonomer is an alpha olefin.

18. An ethylene copolymer comprising in its polyethylene chain trans 1,2-cyclopentanes.

19. The ethylene copolymer of claim 18 wherein at least about 1 percent of all cyclopentane units in said copolymer are trans 1,2-cyclopentane.

20. The ethylene copolymer of claim 19 wherein at least about 10 percent of all cyclopentane units are trans 1,2-cyclopentane.

21. The ethylene copolymer of claim 20 wherein at least about 50 percent of all cyclopentane units are trans 1,2-cyclopentane.

22. The ethylene copolymer of claim 18 also comprising in its polyethylene chain at least one of 1,2 and cis and trans 1,4 noncyclic butadiene comonomer units.

23. The copolymer of claim 22 wherein, of the butadiene comonomer incorporated in said polymer, at least about 50 mole percent is incorporated 1,2 cyclopentane, about 0-50 mole percent is incorporated 1,2, about 0-50 percent is incorporated cis 1,4, and about 0-50 mole percent is incorporated trans 1,4.

24. An ethylene copolymer comprising in its polyethylene chain, as the only cyclopentane unit, trans 1,2-cyclopentane.

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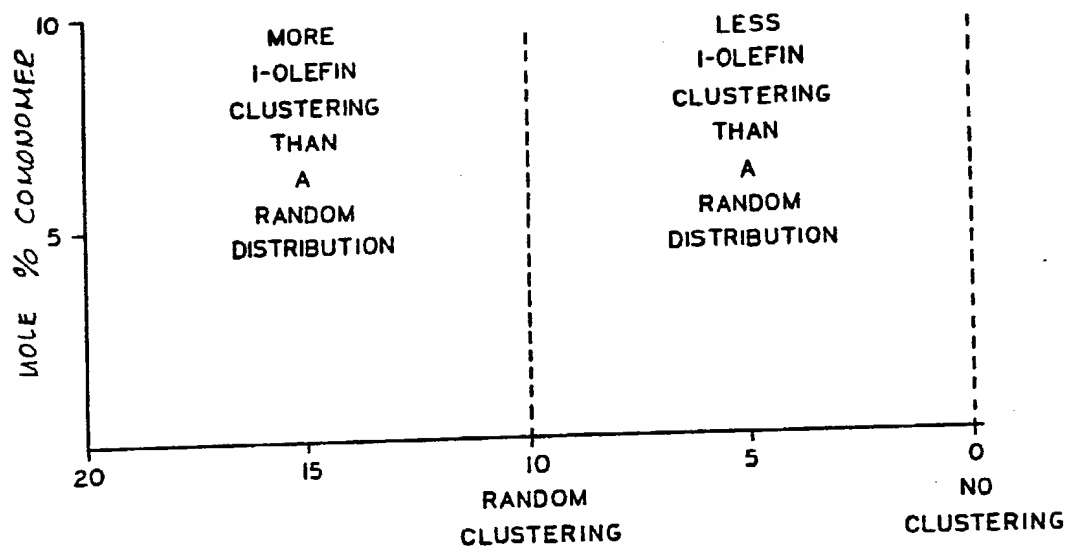


FIG. 1

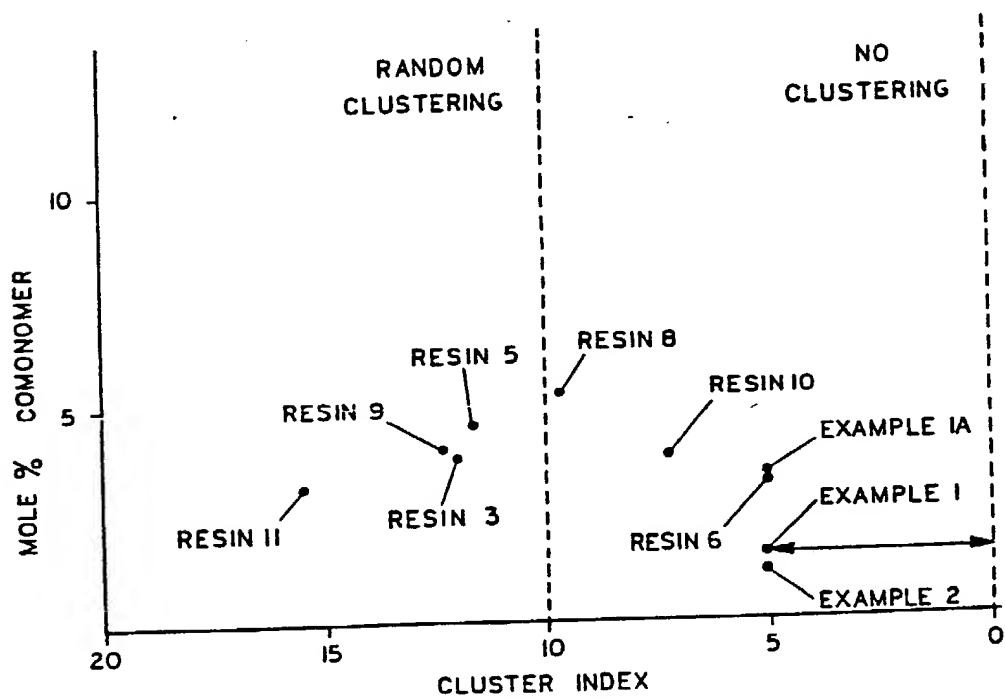


FIG. 2

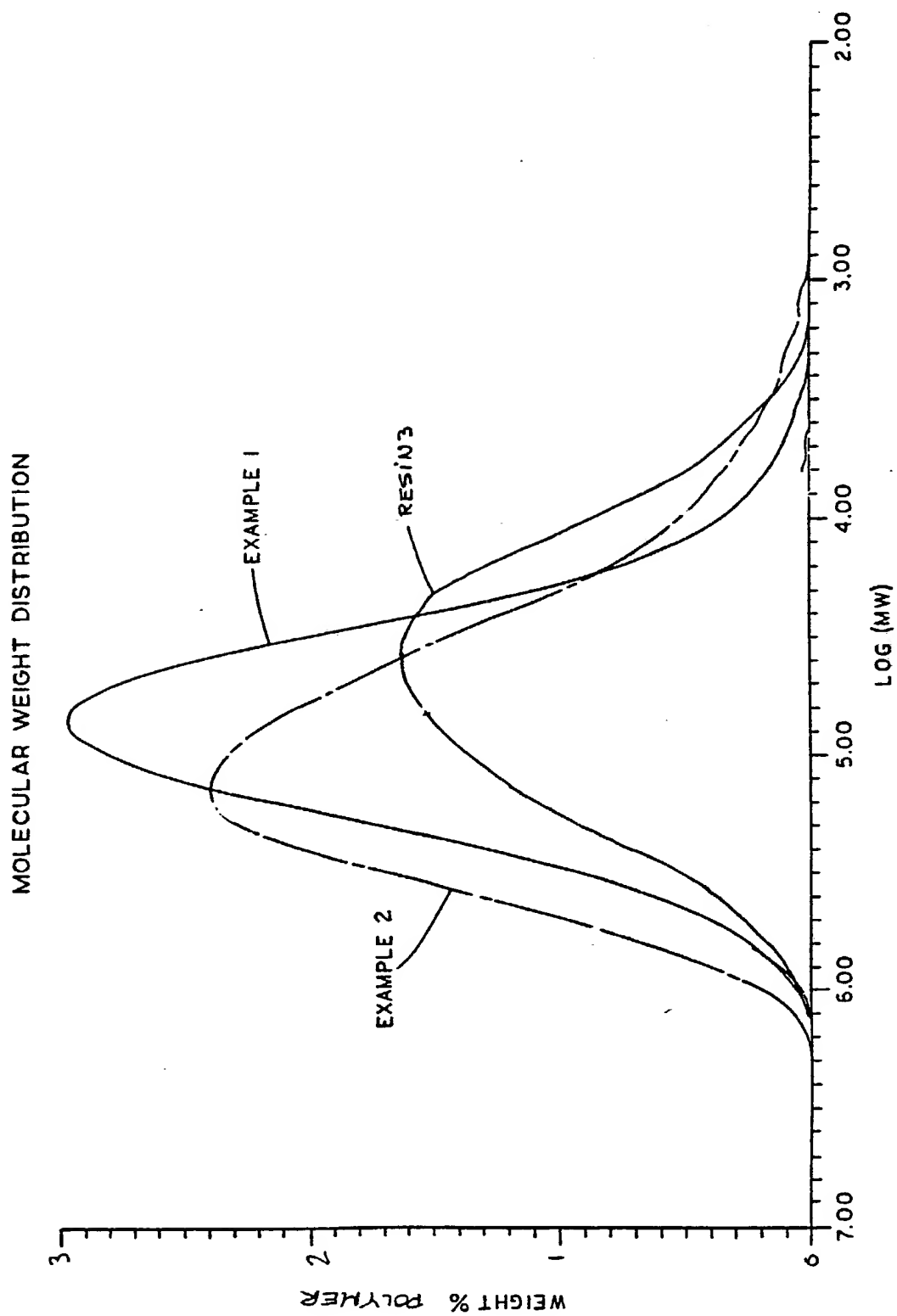


FIG. 3

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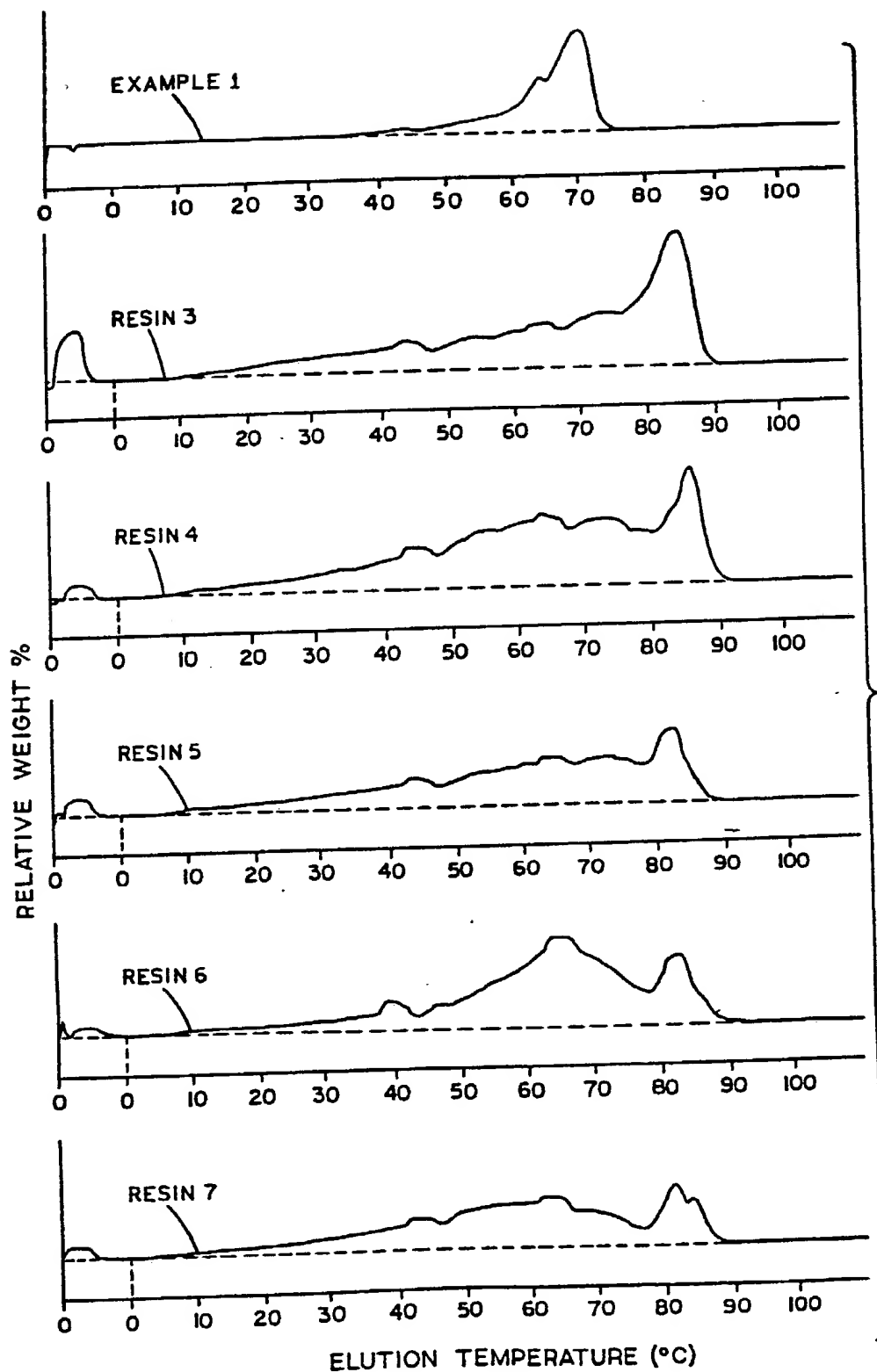


FIG.4

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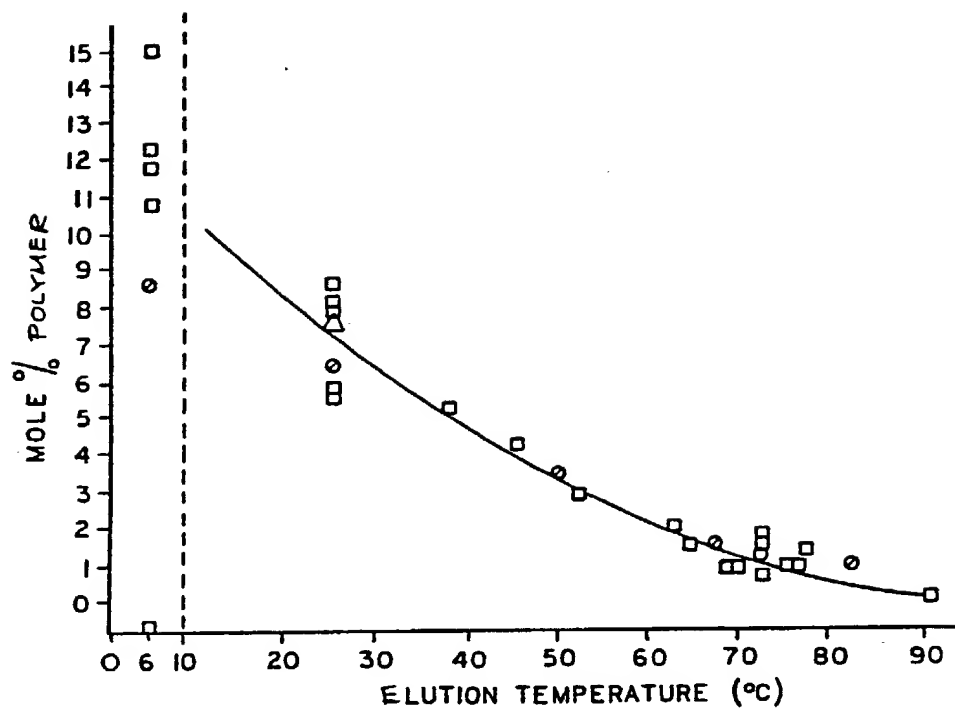


FIG.5

BUTENE	COMONOMER	○
HEXENE	COMONOMER	□
OCTENE	COMONOMER	△

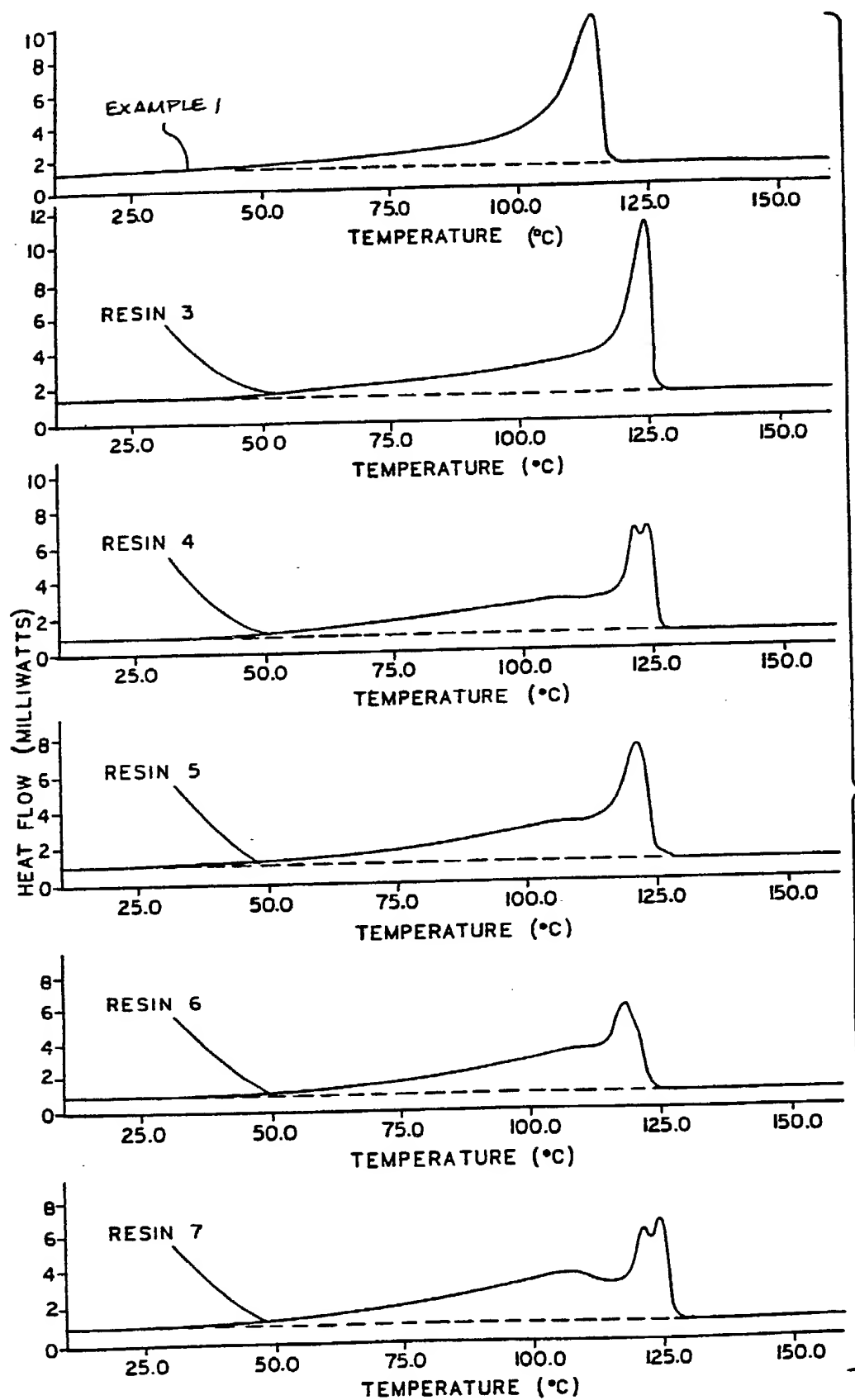


FIG.6

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 87/03297

**I. CLASSIFICATION OF SUBJECT MATTER** (If several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC<sup>4</sup>: C 08 F 210/02; C 08 F 210/16

**II. FIELDS SEARCHED**

Minimum Documentation Searched <sup>7</sup>

Classification System	Classification Symbols
IPC <sup>4</sup>	C 08 F

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched \*

<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT *</b>		
Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	FR, A, 2465755 (ANIC SPA) 27 March 1981 see claim; page 6, line 11 - page 7, line 4	1
--		
A	EP, A, 0048844 (BAYER) 7 April 1982 see claim 1; page 2, line 10 - page 3, line 22	1
--		
A	EP, A, 0069951 (HOECHST) 19 January 1983 see claims 1-8 cited in the application	1
--		
A	EP, A, 0035242 (SINN, HANSJÖRG) 9 September 1981 see claims 1-8; page 13, lines 18-22 cited in the application	1
-----		

- \* Special categories of cited documents: <sup>10</sup>
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "Z" document member of the same patent family

**IV. CERTIFICATION**

Date of the Actual Completion of the International Search

28th April 1988

International Searching Authority

EUROPEAN PATENT OFFICE

Date of Mailing of this International Search Report

06 JUN 1988

Signature of Authorized Officer

P.C.G. VAN DER PUTTEN

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 8703297  
SA 20592

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 24/05/88  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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